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The project objectives are to develop new, low temperature, transition metal catalyzed routes to polysilazanes and related preceramic polymers with controlled rheological properties. Synthetic routes to silicon carbide precursor polymers are also being developed. In addition we are delineating the effects of precursor structure on ceramic product composition (silicon nitride vs silicon carbide vs carbon) as a function of pyrolysis conditions. The utility of using polysilazane ceramic precursors for forming silicon nitride and silicon-carbide nitride fibers and coatings is being explored.

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NEW CATALYTIC ROUTES TO POLYSILAZANE

PRECURSORS TO SILICON NITRIDE AND

RELATED SYSTEMS

Final Technical Report: Project N00014-88-K-0305

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Attention: Drs. Kenneth Wynne and JoAnn Milliken

Introduction

The fabrication of high strength, light weight, ceramic and metal matrix composites (CMCs and MMCs) is an important objective of the Strategic Defense Initiative (SDI) because of the significant impact these materials will have in improving the performance of space-based satellites, their propulsion systems, and the vehicles used for payload delivery. A prerequisite to the manufacture of optimal CMCs and MMCs is the fabrication of high quality, high strength ceramic fibers based on silicon nitride (Si_3N_4), silicon carbide (SiC), silicon carbide nitride (SiCN), or boron nitride (BN) or carbide (B_4C).

Although commercial ceramic fibers with tensile strengths of 350 ksi and 3×10^4 ksi moduli (reported for Nicalon, a SiC based fiber) have been developed, the cost of manufacture is still quite high. Furthermore, the two commercial sources are foreign (Nippon Carbon Co. and Ube Industries) and cannot be relied on for U. S. defense purposes. Considerable time and effort must still be invested to realize technically and commercially viable (low cost) fibers of all classes of ceramics.

In work sponsored by the Strategic Defense Sciences Office through the Office of Naval Research (Contract Nos. N00014-84-C-0392, N00014-85-C-0668, N00014-88-K-0305), we have demonstrated the feasibility of preparing novel polysilazane precursors to Si_3N_4 and SiC/Si_3N_4 using transition metal catalyzed reactions of silanes with amines. We have further demonstrated that these polymers can be used: (1) to form strong ceramic coatings on various metals, glasses, and ceramics; (2) as binders for Si_3N_4 powder and; (3) with proper viscoelastic properties, we have made thin (10-50 μm dia.) ceramic fibers.

Extensive process refinement is still required in the areas of precursor synthesis, delineation of ceramic product evolution with temperature and time and, fiber spinning. Our efforts on contract N00014-88-K-0305 have focussed on: (1) improving catalytic methods for preparing polysilazane and polysilane preceramics; (2) developing methods of characterizing the intermediate materials that form during pyrolytic transformation of precursors into ceramic materials; (3) developing new, more convenient routes to novel preceramics and, (4) processing ceramic coatings and fibers.

As part of the catalytic and preceramic synthesis studies, we have developed a cooperative research program with Professor John Harrod's group at the University of McGill, especially for the development of new synthetic routes to
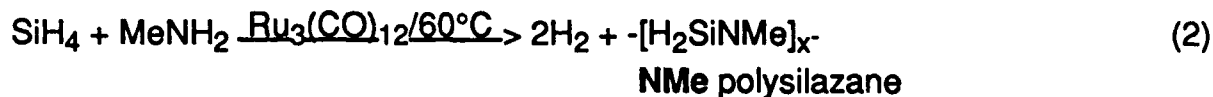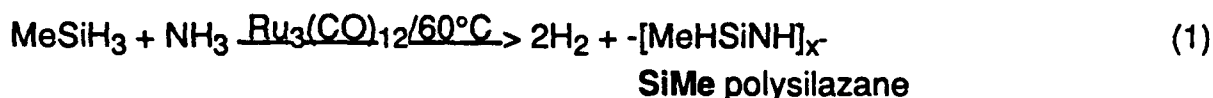
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precursor polymers. We have also developed a cooperative program with Florence Babonneau of the Solid State Chemistry Laboratory at the Univeristé de Pierre et Marie Curie, Paris. Professor Babonneau has, to date, run all of our solid state NMRs gratus. In the following sections, we describe our efforts in these areas.

Research Efforts

The work discussed can be divided into four tasks: (1) Catalyst Development Studies; (2) Precursor Synthesis/Polymerization Studies; (3) Polymer Pyrolysis and Ceramic Characterization Studies and, (4) Synthesis of Novel Precursor Materials. Where possible, Appendices are attached that provide detailed descriptions of the work discussed in the body of the report.

<u>Task 1. Catalyst Development Studies</u>.

Our previous efforts to synthesize Si_3N_4 and SiCN precursors centered on the use of homogeneous ruthenium catalysts to promote dehydrocoupling as illustrated in (1) and (2):[1-8]

$$MeSiH_3 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C} 2H_2 + -[MeHSiNH]_x-$$

(1)

SiMe polysilazane

$$SiH_4 + MeNH_2 \xrightarrow{Ru_3(CO)_{12}/60°C} 2H_2 + -[H_2SiNMe]_x-$$

(2)

NMe polysilazane

Because ruthenium is a very rare metal and is likely to promote Si_3N_4 oxidation at high temperatures,[9,10] our catalyst development objectives have been directed primarily at eliminating its use in reactions such as (1) or (2). Our initial efforts centered on improving the ruthenium catalyst's activity to reduce overall dependence on ruthenium. We were successful in developing a new catalyst, "Active Ru Cat", which is prepared as shown in reaction (3):[7d]

$$RSiH_3 \xrightarrow{Ru_3(CO)_{12}/90°C} "Ru" + SiH_4 + R_2SiH_2$$

(3)
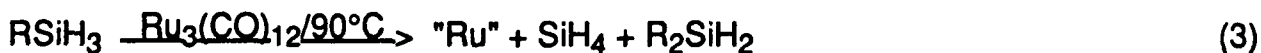
We have now determined (see Appendices I and II) that it is possible to totally supplant the need for ruthenium through the discovery of a titanium catalyst, based on dimethyltitanocene (η^5-$C_5H_5)_2TiMe_2$, that permits us to

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catalyze the polymerization of hydridosilazanes and hydridosiloxanes. This catalyst exhibits much higher catalyst activity than Ru making it useful at room temperature (and below) in very low concentrations. Furthermore, the small amount of Ti that remains in the resulting preceramic will turn into the refractory materials, TiC or TiN on heating. Thus, the titanium catalyst is extremely attractive for preparing useful polysilazanes precursors. The sequence of events that led to our discovery of the utility of Ti catalyzed polymerization is as follows.

Previous work in the Harrod group established that the titanocene catalyst is exceptionally active for dehydrocoupling silanes, reaction (4), and gives well defined (x ≈ 1-10) oligomeric products when R > Et.[11-13] Reaction (4) would be

$$RSiH_3 \xrightarrow{\quad Cp_2TiMe_2/20°C \quad} H_2 + -[RSiH]_x- \qquad (4)$$

extremely useful for preparing simple oligosilanes as reactants for the synthesis of novel polysilazane preceramics, if one could produce oligosilanes with low molecular weight substituents such as R = Et, Me or H, because polymers containing these substituents are likely to give the highest ceramic yields. Furthermore, the -[MeSiH]$_x$- derivative, with a 1:1 Si:C stoichiometry might be an ideal precursor to SiC. Unfortunately, attempts to prepare polysilanes where R = Et, Me or H, using titanocene catalysts, led, until recently (see below), only to intractable, crosslinked polymers.[13] Thus, one recent objective has been to develop new dehydrocoupling catalysts that are actually less reactive with the R = Et, Me or H silanes.

A second unfortunate problem with the $(\eta^5-C_5H_5)_2TiMe_2$ catalyst is that it is not stable even at -20°C. It decomposes autocatalytically via what is apparently a free-radical process. This problem has been partially solved by our finding that catalyst solutions in hexane will remain stable in the absence of light if stored at liquid N_2 temperatures.

A third severe problem that we originally faced in attempting to use the titanocene catalyst for the synthesis of polysilazanes via reaction (1) was that it was inactive. All attempts, in both research groups, to obtain polymerization either with NMe or SiMe polysilazanes or simple model compounds failed. These results were extremely disheartening and only by pure accident were we able to circumvent this problem.

As an outgrowth of a small program sponsored by IBM, we expored the utility

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of dimethyltitanocene for the catalytic redistribution of methylhydrido-
siloxanes (**SiO**), reaction (5), as a method of making methylsilsesquioxane,
$[MeSi(O)_{1.5}]_x$, precursors to SiC/SiO_2 composites. Details of these studies are

$$-[MeHSiO]_x- \xrightarrow{\quad Cp_2TiMe_2/20°C \quad} 1/3MeH_3 + 2/3-[MeSi(O)_{1.5}]_x- \qquad (5)$$

presented in Appendices I-IV.

In the course of these studies, we attempted to make block copolymers of
SiO with the SiMe or NMe oligosilazanes. We expected that the ceramic yields
for a 1:1 mixture of SiMe:SiO would be the arithematic mean of the ceramic
yields of both polymers. The ceramic yield of the polymer produced in (5) under
N_2 is 75-80% and that for the SiMe oligosilazane, which does not react
catalytically with titanocene, is 37%. The expected ceramic yield for a 1:1
SiO:SiMe mixture should be ≈ 55%. To our surprise, the ceramic yield obtained by
treating a 1:1 mixture of $[MeHSiO]_x:[MeHSiNH]_y$ with the titanocene catalyst was
72-74%.

We now find that dimethyl titanocene will polymerize, 1:1, 9:1, 19:1 and even
50:1 mole:mole mixtures of SiMe/SiO to give initially a very viscous liquid
which eventually crosslinks to form a rubber and then a glassy material in 1-20
h at room temperature. The ceramic yields for all of the mixtures run from 60
to 75%. The chemical analysis of the 800°C ceramic product from the 19:1
mixture shows that it is primarily silicon nitride with some silicon oxynitride
and carbon. We therefore suspect that the titanium catalyst will work on the
polysilazanes without added polysiloxane if the true active catalyst
intermediate in reaction (5) is employed. Of note here is that Si_2ON_2 has been
shown to be a reasonable high temperature alternative to silicon nitride.[1,14,15]

We have spent some time in exploring the utility of vanadocene (Cp_2V) and
zirconocene (Cp_2ZrMe_2) catalysts for many of the dehydrocoupling polymer-
zation reactions. We now find that the zirconocene catalyst is very effective
for polymerizing $MeSiH_3$ an excellent precursor to SiC, as we will discuss in the
next section.

Task 2. Precursor Synthesis/Polymerization Studies. The work in this Task,
emphasized the development of new synthetic routes to known precursors
especially, SiC, BN and B_4C and; establishing likely mechanism(s) for Ti
catalyzed polymerization of these precursors. We have also explored to some

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extent the utility of the above mentioned zirconocene catalyst.

Work in the Harrod group as well as by others permits us to suggest two reasonable mechanisms for polysilane polymerizations as discussed in Appendix II. Unfortunately, it is still too early to say that these mechanisms bear any resemblance to those that occur during Ti promoted redistribution of polyhydridosiloxanes and polyhydridosilazanes.

The Harrod group have now discovered that Cp_2V and Cp_2ZrMe_2 are considerably less active for reaction (4) than Cp_2TiMe_2 which permits them to synthesize tractable low molecular weight polymers by dehydrocoupling polymerization of $MeSiH_3$. The GPC shown in Figure 1, indicates a bimodal distribution where the lower weight peak can be attributable to cyclo-polysilanes. The overall $M_n \approx 1,400$ D and $M_w \approx 10K$ D. We have examined the pyrolytic conversion of this material into SiC by heating to selected temperatures and recording MAS NMR and DRIFTS. This compound (see next section) gives almost pure, crystalline SiC at temperatures of 900°C.

Task 3. Polymer Pyrolysis and Ceramic Characterization Studies. In Task 3, we have extended our studies on the chemical and physical processes that are involved in the transformation of precursors into ceramics. Appendix V provides an example of the amount of information that can garnered by coupling DRIFTS with TGA, chemical analysis, and MAS NMR. We are in the process of writing manuscripts with similar analyses for the NMe and SiMe polysilazanes and, for the polymethylsilane precursor. A brief overview of the details of this work are as follows.

Figure 2 shows the solid state ^{29}Si NMR of the SiMe polymer as it is heated to selected temperatures under N_2. At the lowest temperatures, it is a polymer with a single, clean peak at $\approx$ -35-37 ppm. Between 400 and 600°C the polymer is converted to an amorphous ceramic material as indicated by the shift in peak position and its broadening which is an indication of the braod distribution in the types of ^{29}Si magnetic environments. Of importance is that even at 800°C, the material consists of a mixture of Si_3N_4 and an a material that is clearly not SiC but SiCN.

Figure 3 shows similar spectra for the NMe polymer. Below 400°C the material exhibits spectra in accord with its polymeric nature. Above 600°C it is a ceramic and at 800°C, the ^{29}Si spectra indicate "pure" Si_3N_4 with little or no contribution from an SiCN species, despite the presence of up to 20 wt % carbon.

Figure 1. GPC of Polymethylsilane, -[MeSiH]$_x$-. Column calibrated against a polystyrene standard.

Reaction Time: 9 days
Reaction Temp: RT

MeSiH$_3$ Pressure: 125 psi

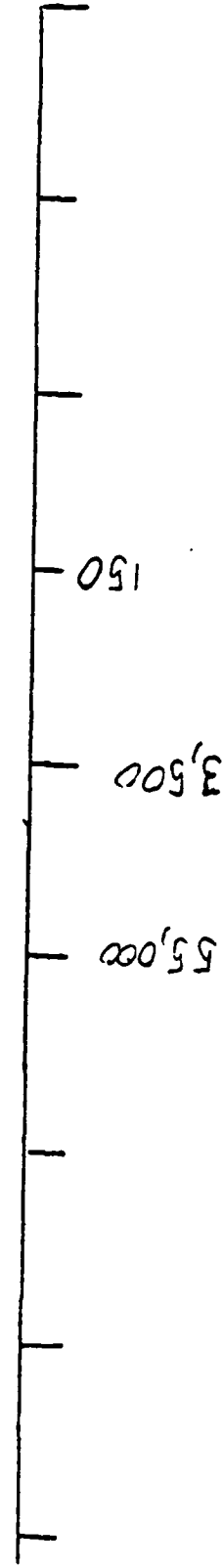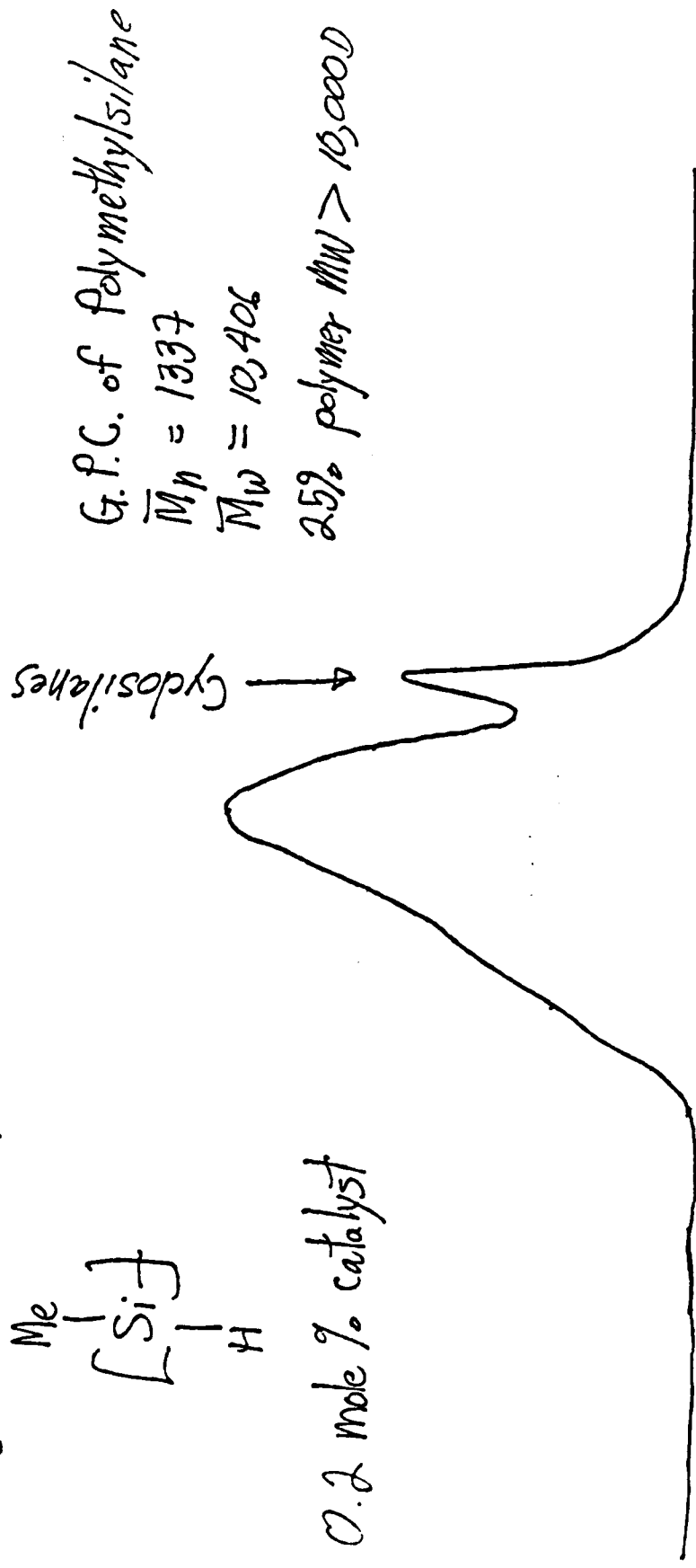$$\left[\begin{array}{c} Me \\ | \\ Si \\ | \\ H \end{array} \right]$$

0.2 mole % catalyst

G.P.C. of Polymethylsilane
$\overline{M}_n = 1337$
$\overline{M}_w = 10,406$
25% polymer MW > 10,000

Cyclosilanes →

55,000   3,500   150

Figure 2. ^{29}Si Spectra for -[MeHSiNH]$_x$- at 25°C and Pyrolyzed to 400, 600, 800 and 1000°C in N$_2$. Heating rate of 5°C/min.
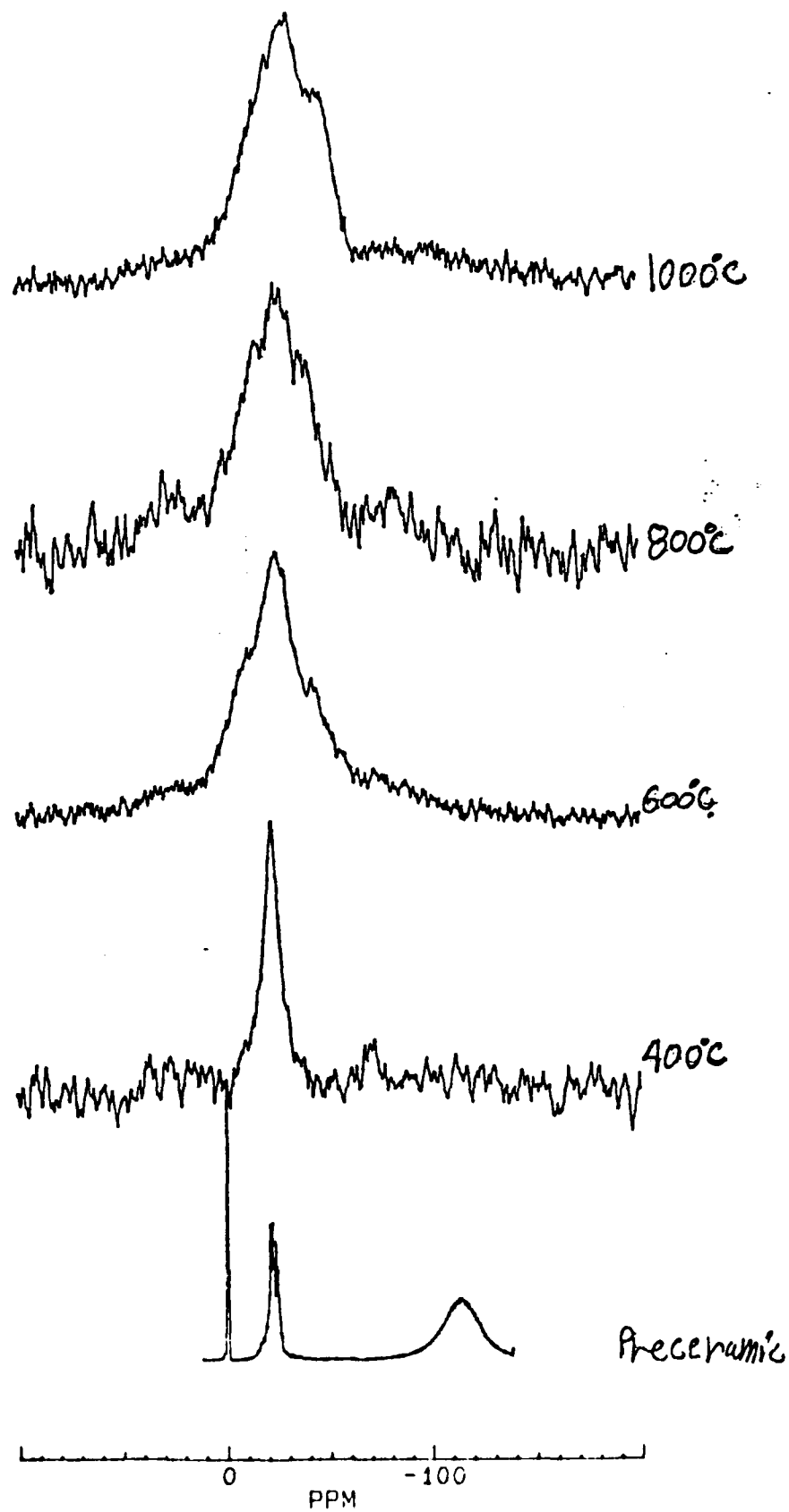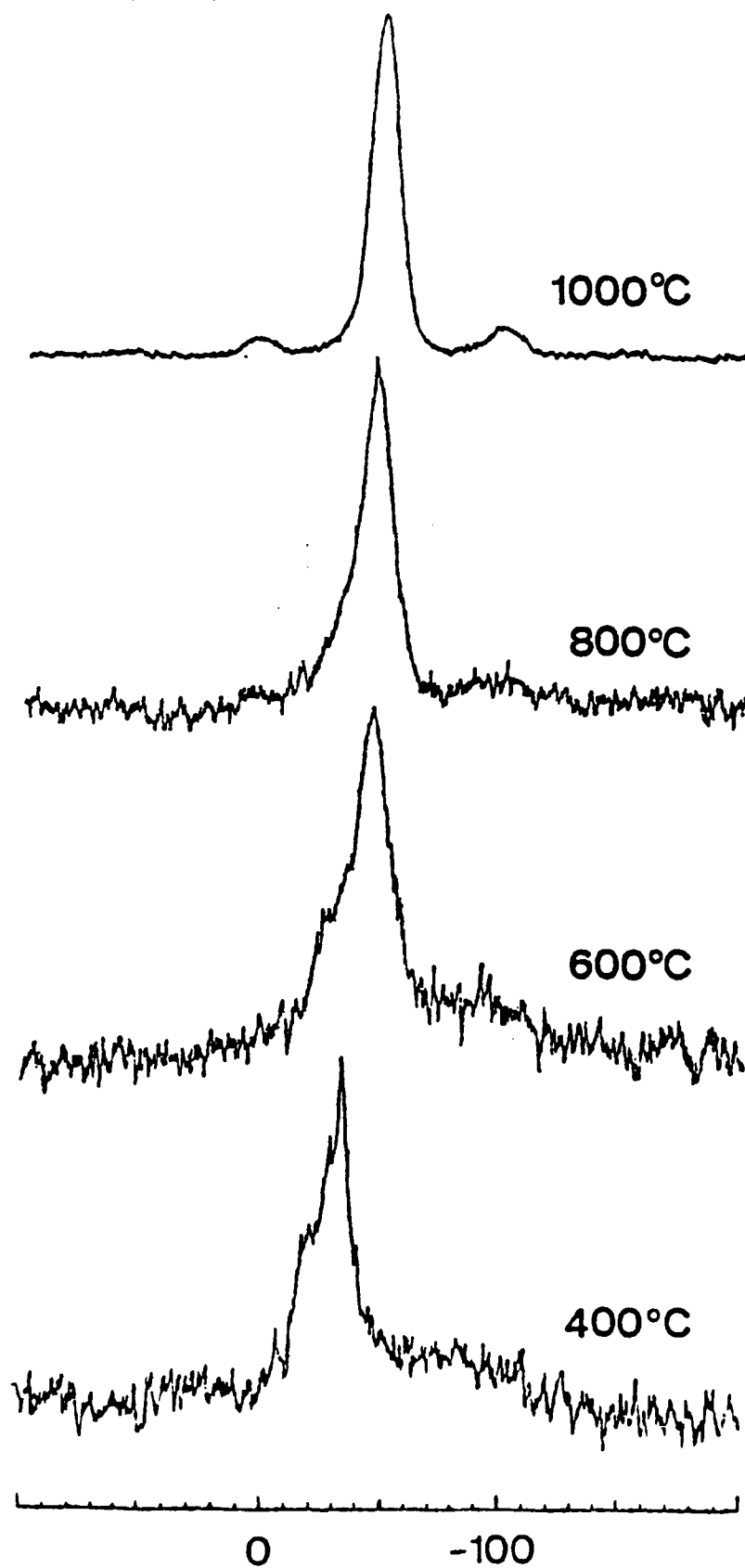
Figure 3. ^{29}Si MAS Solid State NMR of NMe Pyrolyzed to 400, 600, 800, and 1000°C. Note the formation of amorphous silicon nitride (-46 δ) above 400°C. There is no evidence for the formation of SiC which should exhibit a signal at about (-25 δ).

Preliminary small area electron diffraction studies (by TEM) of this material indicate that it is at least partially nanocrystalline at temperatures of below 1000°C. Thus, there are exceptional differences in the products of isostructural precursors.

Our studies with the polymethylsilane precursor, -[MeSiH]$_x$-, are even more rewarding. The solid state ^{29}Si NMR (Figure 4 and 5) reveals that it is transformed from polymer to ceramic at or below 400°C and is transformed into crystalline SiC at 900°C. The DRIFT spectra (Figure 6) suggest that it is partially hydrogenated SiC at temperatures of 600-800°C. Chemical analysis indicates, within the error limits of analysis, that the material is quite pure SiC ($SiC_{0.9}H_{0.05}O_{0.07}$), perhaps the purest SiC produced by such a simply prepared precursor. Recall that $MeSiH_3$ is the byproduct of the redistribution reaction, reaction (5).

Partially hydrogenated SiC produced by CVD is used as a photovoltaic to power hand-held calculators. However, our material could be produced by a spin-on process.

<u>Task 4. Synthesis of Novel Precursor Materials</u>. One of the primary problems associated with the synthesis of preceramic polymers is the relative expense of the simple starting materials. Unfortunately, very few starting materials are available for the synthesis of Si containing preceramics. Furthermore, these starting materials are all derived from one simple set of high temperature chemical reactions. In this task, we have attempted to develop entirely new chemistry for the synthesis of silicon containing preceramics directly from silica, SiO_2.

Currently, all Si products derive from carbothermal reduction of SiO_2 to silicon metal:

$$SiO_2 + 2C \xrightarrow{\hspace{0.5em} 1200°C \hspace{0.5em}} Si + CO + CO_2 \tag{6}$$
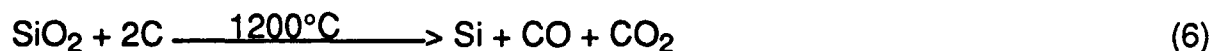
The resulting silicon (90-98% purity) must then be further processed to make other products. For example, fumed silica for optical glass is made by reacting the Si metal from reaction (6) with Cl_2 or HCl to make $SiCl_4$ which can then be burned:

$$Si + 2Cl_2 \longrightarrow SiCl_4 \tag{7}$$

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Figure 4. ^{29}Si Spectra for -[MeSiH]$_x$- at 25°C and Pyrolyzed to 400 and 500°C in N$_2$. Heating rate of 5°C/min with a one hour hold at each temperature.
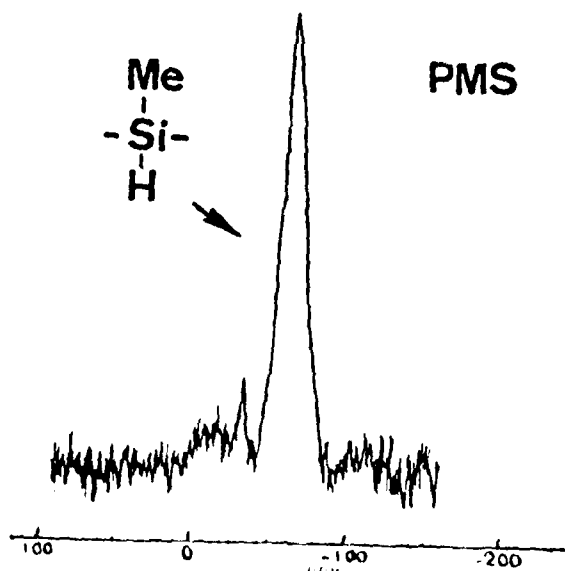
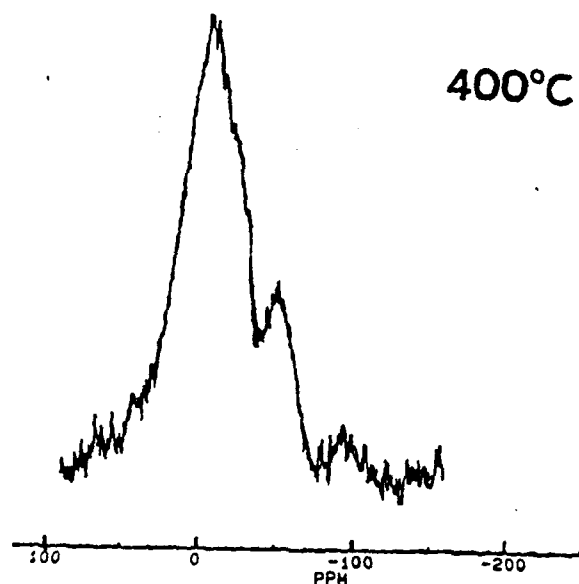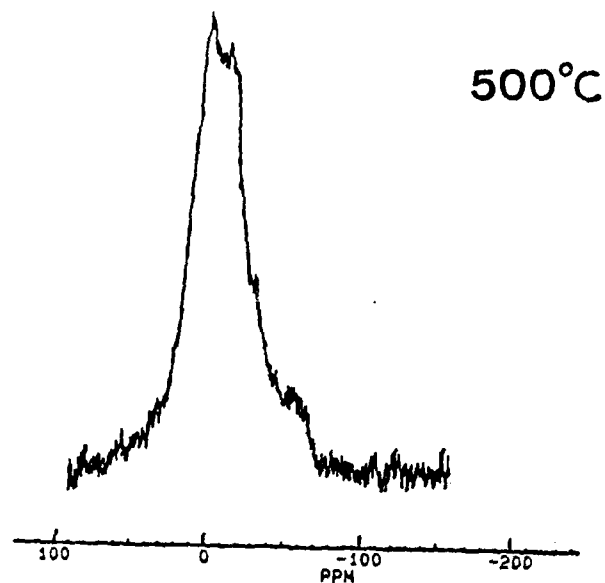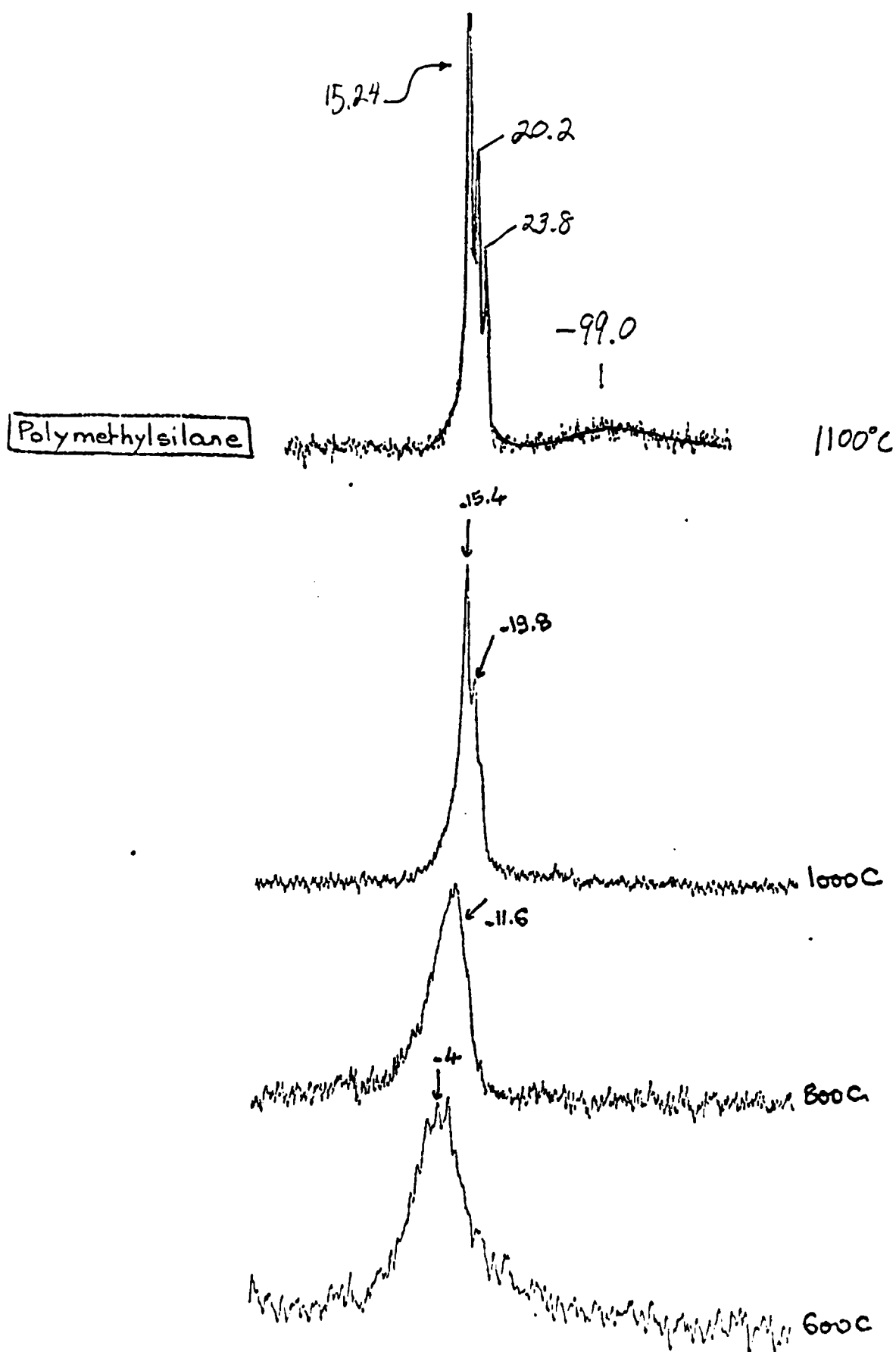**Figure 5**. ^{29}Si Spectra for -[MeSiH]$_x$- Pyrolyzed to 600, 800, 1000 and 1100 in N_2. Heating rate of 5°C/min with a one hour hold at each temperature.
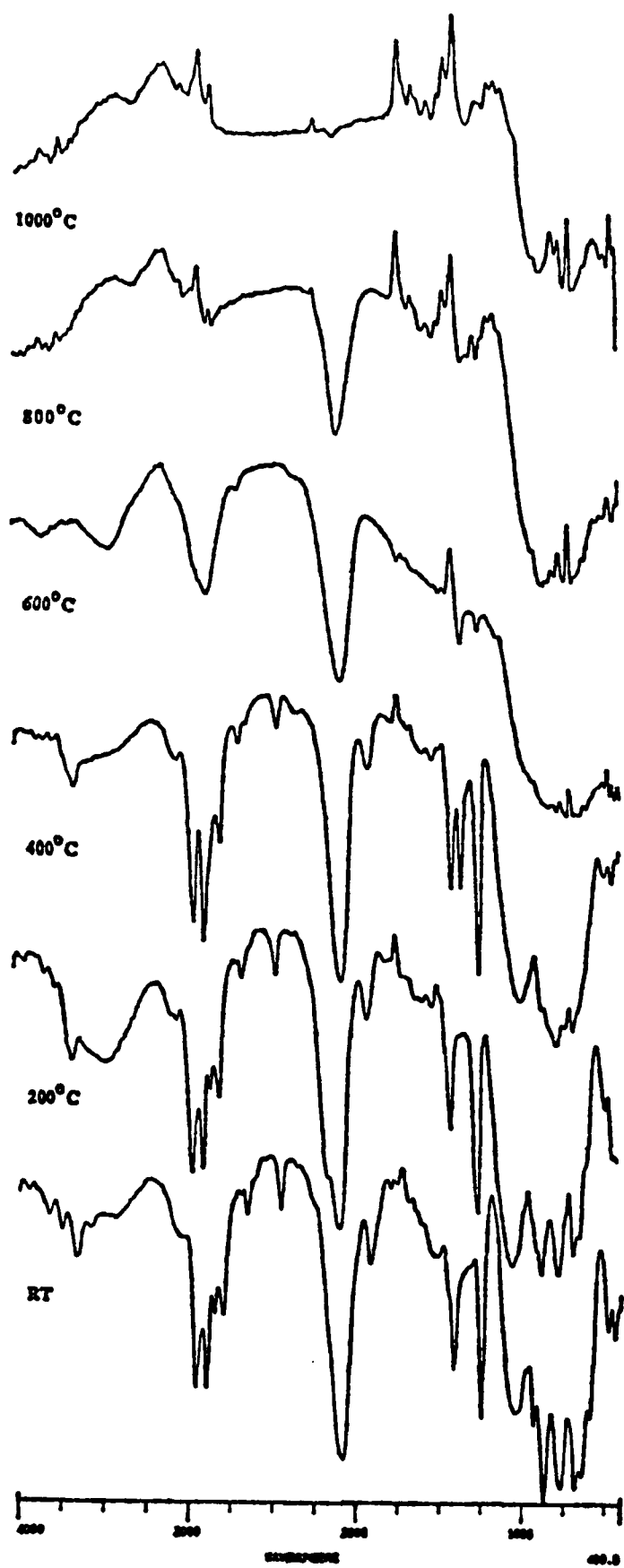
Figure 6 DRIFT Spectra of -[HSiMe]$_x$- Heated to Selected Temperatures

$$Si + HCl \longrightarrow HSiCl_3 + SiCl_4 \tag{8}$$

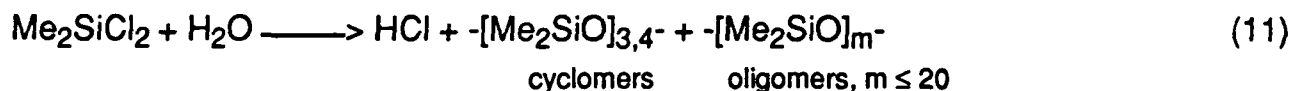$$SiCl_4 + H_2O + O_2 \longrightarrow SiO_2 + HCl + HClO_x \tag{9}$$

Carbothermal reduction requires high heat and specialized equipment. The result is an energy and equipment intensive process. Reaction of Si with chlorine or HCl also requires specialized, expensive equipment to deal with toxic and corrosive materials. Despite these considerable drawbacks, the basic technology derives from the last century and as such, all of the processing problems have been worked out. This, coupled with the economy of scale makes this approach to fumed silica commerically successful.

The production of silicon based chemicals follows somewhat similar chemistry. All silicone polymers derive from the "Direct Process:"

$$RCl + Si \xrightarrow{\underline{Cu/Zn/250\text{-}500°C}} RSiCl_3 + R_2SiCl_2 + R_3SiCl + ... \tag{10}$$
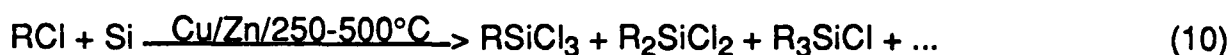
This simple reaction only works well when RCl is MeCl or PhCl. When it is MeCl, the major product is Me_2SiCl_2, which is hydrolyzed and polymerized to give polydimethylsiloxane, the basic silicone polymer:

$$Me_2SiCl_2 + H_2O \longrightarrow HCl + \text{-}[Me_2SiO]_{3,4}\text{-} + \text{-}[Me_2SiO]_m\text{-} \tag{11}$$
$$\qquad\qquad\qquad\qquad\qquad\quad \text{cyclomers} \qquad \text{oligomers, } m \le 20$$

$$\text{-}[Me_2SiO]_{3,4}\text{-} + Me_3SiO^- \longrightarrow Me_3SiO\text{-}[Me_2SiO]_x\text{-}H \tag{12}$$
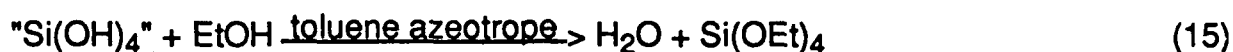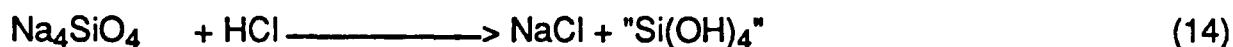
The above six reactions when coupled with standard organic chemistry, some special derivatives and processing procedures provide the basis for the entire silicone and silicon materials industry. It is amazing that there are no alternate methods for producing silicon based polymers.

As discussed above, we have developed a very simple and extremely economical method of transforming SiO_2 into useful, reactive compounds based primarily on ethylene glycol. If properly developed these compounds offer economical access to silicon based chemicals and polymers without recourse to high temperature processing. Furthermore, the polymeric species offer exceptional opportunity to fabricate unique materials including novel zeolites, ceramic fibers, coatings, optical glasses and, ceramic fibers.

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There are few, simple, low temperature methods of chemically modifying silica. One such method is dissolution in base to give sodium silicate:

$$NaOH + SiO_2 \longrightarrow Na_4SiO_4 \tag{13}$$
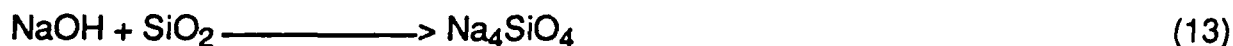
Unfortunately, this reaction has limited application for the formation of useful feedstock chemicals. Recently Kenny and Goodwin[1] have succeeded in esterifying silicic acid, reactions (14) and (15) to form $Si(OEt)_4$, which is

$$Na_4SiO_4 + HCl \longrightarrow NaCl + "Si(OH)_4" \tag{14}$$

$$"Si(OH)_4" + EtOH \xrightarrow{\text{toluene azeotrope}} H_2O + Si(OEt)_4 \tag{15}$$

currently produced by reaction of EtOH with $SiCl_4$. $Si(OEt)_4$ is used commercially to form fumed silica, optical glasses and boules for spinning fiber optics.
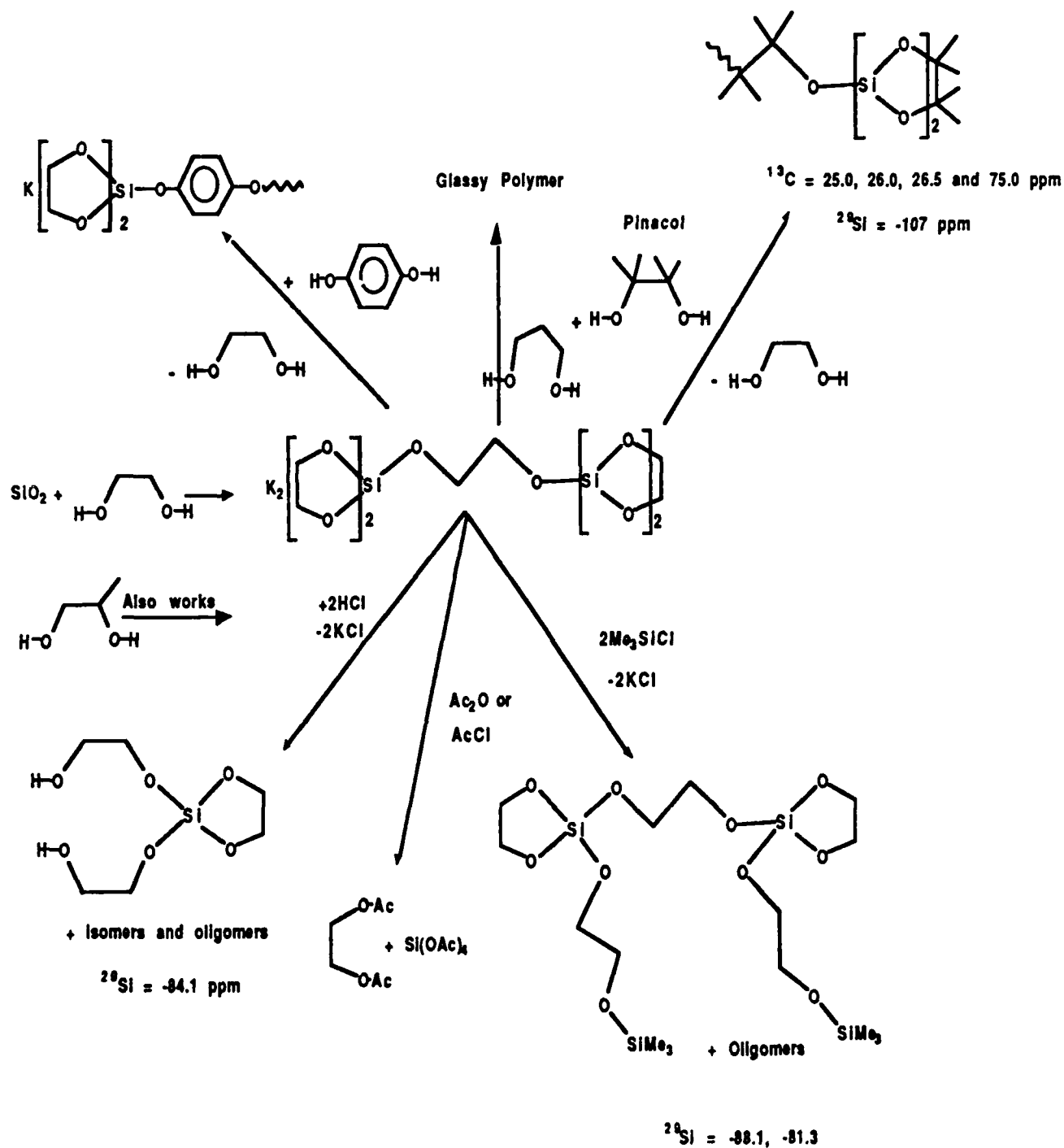
Another method of transforming silica into useful chemicals is based on the reaction of silica with catechol:
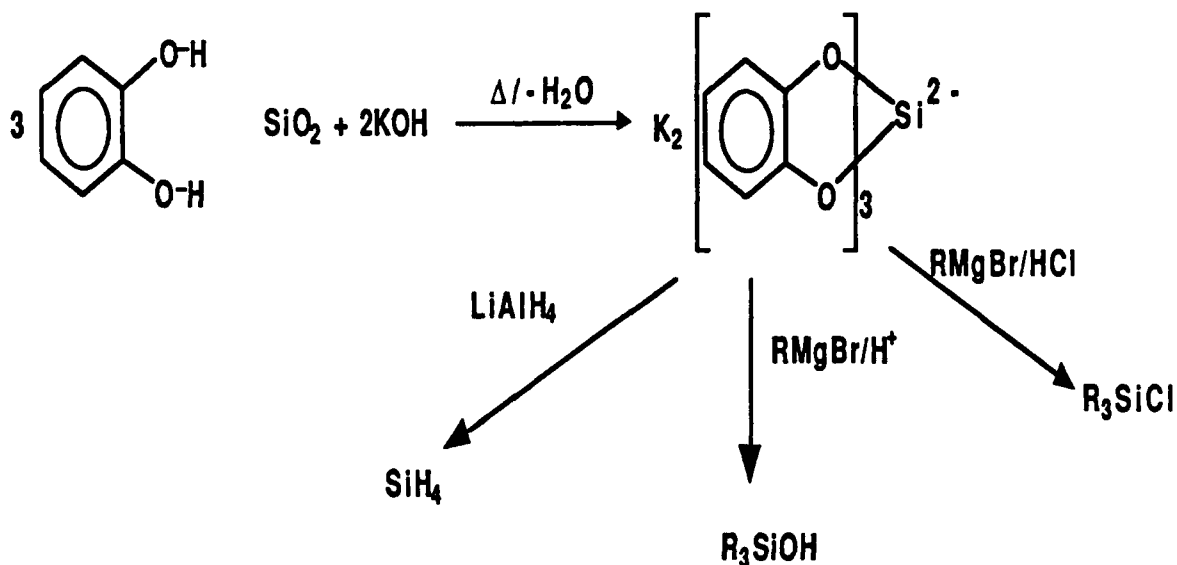
The problem with this approach is that the catechol complex, tris(1,2-dihydroxobenzoato) siliconate, is expensive, too stable and can only be modified under forcing conditions using expensive reagents such as $LiAlH_4$ or RMgBr. Consequently, its utility is limited.

Our approach has been to explore methods of making a more reactive complex of silica using ethylene glycol instead of catechol. We have successfully demonstrated the feasibility of this concept and the utility of the resulting product as shown in the schematic below.

The chemistry shown below has been formalized in 70% of the cases shown. We expect to reduce to practice more of this work in the very near future.

Glassy Polymer

Pinacol

^{13}C = 25.0, 26.0, 26.5 and 75.0 ppm

^{29}Si = -107 ppm

SiO_2 +

Also works

+2HCl
-2KCl

Ac_2O or
AcCl

$2Me_3SiCl$
-2KCl

+ Isomers and oligomers

^{29}Si = -84.1 ppm

+ $Si(OAc)_4$

+ Oligomers

^{29}Si = -88.1, -81.3

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Experimental Section

General.

1. Procedures. All operations were carried out with the careful exclusion of extraneous moisture. Air sensitive materials were manipulated using standard Schlenck and glovebox techniques. ^1H, ^{13}C and ^{29}Si spectra NMR spectra were taken in d^4-methanol and referenced to TMS. All chemicals were purchased for standard vendors and used as received except, the diols which were distilled under nitrogen before use.

2. Equipment. Infrared spectra were recorded on an IBM FTIR-44 spectrophotometer. Nuclear magnetic resonance data were collected on a Varian 300 MHz spectrometer. Elemental analyses were performed by Galbraith Laboratories, in Knoxville, TN.

Materials.

1. Preparation of $K_2Si_2(OCH_2CH_2O)_5$. 13.8 grams of 400 mesh silica gel (0.23 mol) and 14.8 grams (0.26 mol) of potassium hydroxide (85%) were weighed into a 500 mL round bottom flask. 125 mL of freshly distilled (from Mg/MgI_2) EtOH and 250 mL of distilled ethylene glycol were added to the flask and the mixture was heated to boiling. The ethanol fraction was distilled off to remove (by azeotrope) any water formed during the reaction. The mixture was then heated further until the solution appeared homogeneous, partial dissolution of the silica occurred during this period. Distillation was continued to remove the major fraction of the excess ethylene glycol. During distillation, most of the silica dissolves. Upon cooling the remaining colorless liquid turned to a sticky white solid mass. This mass was taken up in 350 mL of freshly distilled methanol and filtered through a celite covered frit. The filtrate was concentrated *in vacuo* to ≈ 20mL after which portions of dry acetonitrile were added slowly to precipitate out a fine white powder. The precipitate was then collected on a glass frit and washed with 3 X 200 mL of acetonitrile. Recrystallization from methanol and acetonitrile/ether resulted in a pure white powder which was vacuum dried. This results in 90g (0.21 mol) of product or 90 % yield. NMR: ^1H, 3.4 ppm (under solvent peak); ^{13}C, 61.1, 64.3 ppm; ^{29}Si, -103.0 ppm. Elemental analysis, calc. (found) %C, 27.53 (27.63); %H, 4.98 (4.64); %Si, 13.60 (12.92); %K 17.84 (17.99); %O by difference, 37.01 (36.81).

2. Preparation of $Li_2Si_2(OCH_2CH_2O)_5$. A procedure similar to that used for the potassium derivative was employed using 5.00 g (0.083 mol) of silica and

1.98 g (0.083 mol) of LiOH. If the "polymeric" portion of the product, that portion which is not immediately soluble, is left stirring for 1-2 days in methanol, then it dissolves quantitatively. The resulting methanol soluble material is recrystallized from methanol and acetonitrile/ether and vacuum dried. This results in 26.2 g (71 mmol) of product or 85 % yield. NMR (CD_3OD): ^1H, 3.4 ppm (under solvent peak); ^{13}C, 61.2, 64.4 ppm; ^{29}Si, -102.9 ppm.

3. Preparation of $Na_2Si_2(OCH_2CH_2O)_5$. Procedures identical to those described for the preparation of the potassium salt were used except 3.33 g (83 mmol) of NaOH were used. Again stirring for 1-2 days in methanol results in complete dissolution The methanol soluble material can be recrystallized as above and dried in vacuum. The yield is 26 g (75 mmol) or 90 %. NMR (CD_3OD): ^1H, 3.36 ppm; ^{13}C, 63.2 ppm; ^{29}Si, -103.3 ppm.

4. Preparation of $CsSi_2(OCH_2CH_2O)_2(OCH_2CH_2OH)$. Procedures identical to those described for the preparation of the potassium salt were used except 8.74 g (83 mmol) of CsOH were used. The product in this instance was entirely soluble in ethanol. The product was precipitated out by addiiton of acetonitrile. Although almost all of the silica dissolved, the isolated yield was only % 53. NMR (CD_3OD): ^1H, 3.4 ppm (under solvent peak); ^{13}C, 63.2 ppm; ^{29}Si, -103.1ppm. Elemental analysis, calc. (found) %C, 20.72 (21.06); %H, 3.63 (3.83); %Si, 8.58 (8.21); %Cs 39.38 (38.84); %O by difference, 27.32 (27.06).

5. Exchange of Pinacol for Ethylene Glycol. 1.5 g (3.46 mmol) of $K_2Si_2(OCH_2CH_2O)_5$ are mixed with 80 ml of freshly distilled pinacol (added as a solvent). The reaction mixture is then heated under N_2. The mixture melts, the siliconate dissolves and heating is continued until 65 ml of a mixture of ethylene glycol and pinacol are distilled off. On cooling the remaining liquid becomes a white solid. Excess pinacol is washed away using 2x50 ml of acetonitrile. The remaining white material is then dissolved in methanol and recrystallized as above. The yield is essentially quantitative. NMR (CD_3OD): ^1H, 3.4 ppm (under solvent peak); ^{13}C, 75.8, 26.5, 25.9 ppm; ^{29}Si, -109 ppm.

6. Exchange of 1,2-Propanediol for Ethylene Glycol. 5.0 g (11.5 mol) of $K_2Si_2(OCH_2CH_2O)_5$ are mixed with 50 ml of freshly distilled propandiol (added as a solvent). The reaction mixture is then heated under N_2. The siliconate

dissolves and heating is continued until a 35 ml mixture of ethylene glycol and propanediol is distilled off. The remaining solution is syringed into 50 ml of cold diethyl ether. The product collects as an oil at the bottom of the flask. The oil is cannulated into a 50 ml Schlenck flask and dried *in vacuo* to a clear glassy solid. This solid is dissolved in 15 ml of MeOH and syringed into 70 ml of acetonitrile to give a precipitate which is filtered off on a medium frit. NMR (CD$_3$OD): ^{1}H 1.75 quintet, 1.74 quintet, 3.35 s, 3.66 triplet, 3.67 triplet, 5.13 s ppm; ^{13}C, 60.0 and 36.3 ppm; ^{29}Si, -107.2 ppm.

7. Exchange of PEG$_4$ for Ethylene Glycol.

5.0 g (13.5 mmol) of Li$_2$Si$_2$(OCH$_2$CH$_2$O)$_5$ are mixed with 50 ml of ethylene glycol. The stirred soluton is heated under N$_2$ until all of the lithium salt dissolves. 40 ml freshly distilled PEG$_4$ (tetraethylene glycol) are then added. The excess ethylene glycol is distilled off to give a clear yellow solution. 20 ml of PEG$_4$ was removed by distillation at reduced presurre. 40 ml of EtOH are then added and acetonitrile is added to precipitate a crude product which is filtered and dried *in vacuo*. To date the crude material has been characterized only by ^{13}C NMR (CD$_3$OD): ^{13}C, 73.6, 71.3, 64.3 and 62.1. The latter two peaks may indicate some ethylene glycol remains.

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List of Publications for Project N00014-88-K-0305

1. "New Catalytic Routes to Preceramic Polymers: Ceramic Precursors to Silicon Nitride and Silicon-Carbide Nitride", K. A. Youngdahl, R. M. Laine, R. A. Kennish, T. R. Cronin, and G. A. Balavoine, in Better Ceramics Through Chemistry III, Mat. Res. Symp. Proc. Vol. **121**, C. J. Brinker, D. E. Clark, and D. R. Ulrich Eds. (1988) 489.

2.   "Structure/Reactivity Relationships of Polysilazane Preceramics." K. A. Youngdahl, J. A. Rahn, R. M. Laine, R. A. Kennish and G.A. Balavoine. Fourth Internat. Conf. on Ultrastructure Processing of Glasses, Ceramics, Composites and Polymers, Symp. Proc. in Press.

3. "Synthesis of Inorganic Polymers as Glass Precursors and for Other Uses. Preceramic Block or Graft Copolymers as Potential Precursors to Nanocomposite Materials", K. A. Youngdahl, M. L. Hoppe, R. M. Laine, J. A. Rahn and J. F. Harrod; Fourth Inter. Conf. on Ultrastructure Processing

of Glasses, Ceramics, Composites and Polymers, Symp. Proc. in press.

4. "Transition Metal Catalyzed Synthesis of Oligo- and Polysilazanes and Their Use as Precursors to Silicon Nitride Containing Ceramic Materials", R. M. Laine, Plat. Met. Review (1988) **32**, 64.

5. "Synthesis and High Temperature Chemistry of Methylsilsesquioxane Polymers Produced by Titanium Catalyzed Redistribution of Methylhydridooligo- and polysiloxanes." R. M. Laine, K. A. Youngdahl, F. Babonneau, J. F. Harrod, M. L. Hoppe, J. A. Rahn, Chem. of Mater. (1990) **2**, xx.

6. "The Catalytic Synthesis of Inorganic Polymers for High Temperature Applications and as Ceramic Precursors", J. A. Rahn, R. M. Laine and Z-F. Zhang, in "Polymer Based Molecular Composites", Mater. Res. Soc. Sym. Proc. Vol. **171**, 1990 in p. 31.

7. "Transition Metal Catalyzed Synthesis of Organometallic Polymers" R. M. Laine in Aspects of Homogeneous Catalysis, Vol **7**, R. Ugo ed., Kluwer publ. in press.

8. "Catalytic Synthesis of Polymethylsilsesquioxanes", Richard M. Laine, Jeffrey A. Rahn, Kay A. Youngdahl and John F. Harrod, Am. Chem. Soc. Symp. Series in press, paper presented at the Am. Chem. Soc. Meeting; April 1990, Boston, MA. Catalysis Secretariat

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Appendices:

15

Synthesis of Inorganic Polymers as Glass Precursors and for Other Uses. Preceramic Block or Graft Copolymers as Potential Precursors to Nanocomposite Materials

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Preceramic block or graft copolymers may offer entrée into nanocomposite ceramics provided the two homopolymers are immiscible and one can carefully control the size of the blocks or grafts. We are exploring the possibility of making copolymers from methylsilsesquioxane, $-[MeSi(O)_{1.5}]_x-$, (SiO), a precursor to "black glass" and the polysilazane, $-[MeHSiNH]_x-$, (SiMe), a precursor to silicon carbide nitride. Our initial efforts have been directed towards delineating the chemical transformations that SiO, prepared by room temperature catalytic redistribution of $-[MeHSiO]_x-$ using Cp_2TiMe_2 as the catalyst (0.1 wt %), undergoes as it is heated to 900°C in N_2. We find that although Cp_2TiMe_2 will not catalyze the redistribution of SiMe at room temperature; in the presence of even small amounts of $-[MeHSiO]_x-$, it is an active catalyst precursor and a copolymer can be formed. Spectral and chemical composition studies on the pyrolysis products of the copolymers and SiO are described.
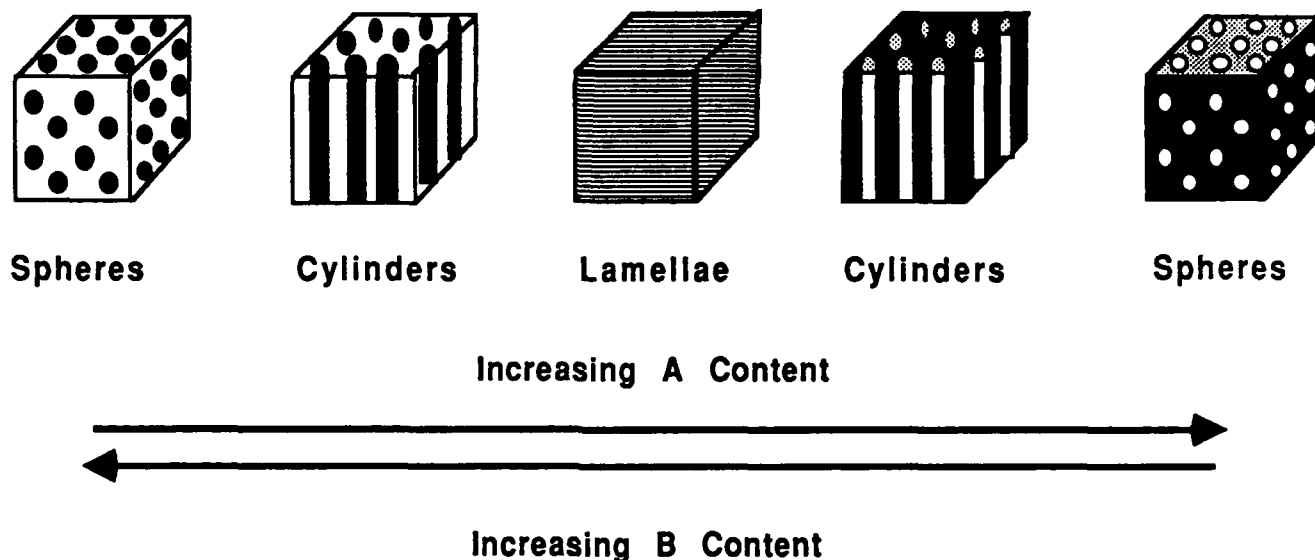
1. Introduction

The alloying or blending of one polymer with another is often used as a means of enhancing the physical and chemical properties of one or both polymers. Mixing is obtained by dissolution in a common solvent or by melt-mixing. This "co-mingling" of properties is effective only if the two polymers are compatible and do not segregate (on a macroscopic level) upon heating, with time, or segregate only under a specific (narrow) set of conditions.

Segregation in polymer blends or alloys can sometimes be avoided through the synthesis of block or graft copolymers wherein oligomeric chains of polymer A are chemically bonded to chains of polymer B. However, if the physical properties of A and B are quite disparate, then segregation can occur on a mesoscopic (nano) scale. In some instances, mesoscopic segregation can be beneficial, especially for "toughening" purposes.

For example, the block copolymerization of A with B or grafting of A to B, can lead to the

formation of unique, three dimensional microstructures, as illustrated by Scheme 1[1]. Thus, if A is the minority phase in a block or graft copolymer of A and B, then one obtains a segregated structure, as shown below, in which spheres of A form in a matrix of B. The converse is true if small quantities of B oligomers are copolymerized with A oligomers. As the mole fraction of A oligomers

| Spheres | Cylinders | Lamellae | Cylinders | Spheres |

Increasing A Content

Increasing B Content

Scheme 1. Effect of Changes of Composition on the Microstructure of a Block Copolymer.

increases relative to B oligomers then one obtains progressively: spheres, cylinders and then lamellar structures when A ≈ B. These structures offer considerable potential for "toughening" provided certain design criteria are met[1].

The diameter and definition of the spherical and cylindrical microstructures are controlled by the polymer, the chain lengths and the polydispersity of the minority component. Likewise, the thickness and definition of each lamella is controlled by the number of monomer units in the chain segments of A and B as well as the polydispersity. Furthermore, A must be immiscible in B. If these design criteria are met, it should be possible to tailor the microstructures of block or graft copolymer shapes and thereby obtain precise control of the physical and mechanical properties of the resultant piece.

Extension of the concept of tailored block or graft copolymers to preceramic polymers, offers the unique opportunity to fabricate ceramic shapes wherein one can control the size, configuration and distribution of heterogeneities in the ceramic body by controlling the nanostructural features of the precursor polymer. Thus, small amounts of precursor oligomer A, copolymerized with

oligomers of precursor B should lead to ceramics, following pyrolysis, that have approximately spherical _reinforcing_ heterogeneities. This assumes that the oligomers of A are not miscible with B and that their chain lengths and molecular weights are narrowly defined. It also assumes that segregation is maintained during pyrolysis.

To our knowledge, no one has attempted to develop preceramic block or graft copolymers for the express purpose of introducing controlled heterogeneities into the resultant ceramic product. Seyferth et al.[2] have synthesized $-[(MeSiH)_a(MeSi)_b-(MeSiNH)_c(MeSiN)_d(MeHSiNMe)_e]_n-$ graft copolymers to adjust the composition ($SiC:Si_3N_4$) of the final ceramic product. However, with the exception of Seyferth et al., little has been done to develop systems of mixed preceramic polymers either by chemical linkage (grafting or copolymerization) or by physical mixture, despite the potential for forming nanocomposite materials.

The long term objective of the work discussed here is to explore the use of preceramic copolymers as a means of preparing ceramic materials with controlled heterogeneities--nanocomposite ceramics. However, to achieve this objective it is first necessary to develop two distinct preceramic polymer systems wherein we can exert control of both the macromolecular properties (degree of polymerization, polydispersity, rheology) and pyrolytic selectivity to specific ceramic products. It will also be necessary to establish that physical mixtures and then copolymers of these preceramics will segregate and will, when pyrolyzed, give ceramic products that maintain the preceramic segregation. Furthermore, we must also develop methods of characterizing both the preceramics and the expected amorphous ceramic products so that we can identify the individual product phases. Finally, the choice of both preceramics must be such that on pyrolysis they do not react to form a third ceramic material.

To this end, we are exploring the use of two types of preceramic polymers. One, based on $-[MeHSiO]_x-$, when catalytically polymerized and pyrolyzed to 900°C, gives "black glass" which consists of silica (79% by mole fraction), SiC (20%) and carbon (10%). The second preceramic is the nitrogen analog, $-[MeHSiNH]_x-$ (SiMe), which when pyrolyzed to 900°C gives an amorphous ceramic with an apparent ceramic composition of Si_3N_4 (65% by mole fraction), SiC (25%) and carbon (10%). In this paper, we discuss our preliminary studies on the pyrolysis and characterization of the black glass precursors, and results of our studies on pyrolysis of that precursor with the SiMe polysilazane, $-[MeHSiNH]_x-$. The synthetic and experimental details will be presented elsewhere.

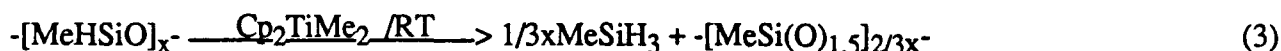## 2. Results and Discussion

Alkyl silsesquioxanes, $-[RSi(O)_{1.5}]_x-$, prepared by sol-gel processing of alkylsiloxanes, $RSi(OEt)_3$, have been studied by Fox et al.[3] as precursors to silicon carbide powders and to

3

$$RSi(OEt)_3 + 1.5H_2O \xrightarrow{\text{catalyst = acid}} 3EtOH + \text{-}[RSi(O)_{1.5}]_x\text{-} \tag{1}$$

silicon carbide reinforced black glass [reaction (1)]. Kamiya et al.[4] have recently described the use of methyl silsesquioxane as a precursor for the processing of nitrided glass fibers. Zhang and Pentano[5] are currently exploring the utility of black glasses as a matrix for the fabrication of graphite fiber composites.

Our recent discovery[6] that dimethyltitanocene derived catalysts can be used to catalyze the redistribution of hydridosiloxanes, reaction (2), at room temperature, prompted us to consider using the same system, as in (3), to produce the silsesquioxane, $\text{-}[MeSi(O)_{1.5}]_x\text{-}$ from $\text{-}[MeHSiO]_x\text{-}$.

$$MeHSi(OEt)_2 \xrightarrow{Cp_2TiMe_2 /RT} MeSiH_3 + MeSi(OEt)_3 \tag{2}$$

$$\text{-}[MeHSiO]_x\text{-} \xrightarrow{Cp_2TiMe_2 /RT} 1/3xMeSiH_3 + \text{-}[MeSi(O)_{1.5}]_{2/3x}\text{-} \tag{3}$$

Furthermore, the tetrameric and pentameric cyclomers of $\text{-}[MeHSiO]_x\text{-}$ or well defined (by D.P. or M_n) linear chain analogs are commercially available. This suggested that these species, when used in conjunction with reaction (3), might serve as a potential second preceramic system with the well studied SiMe polysilazane system[2,7-9] to test the feasibility of the block copolymer approach to nanocomposite structures. Finally, we found that the siloxane precursor was not miscible with either $\text{-}[MeHSiNH]_x\text{-}$ or the isostructural $\text{-}[H_2SiNMe]_x\text{-}$[9].

Methylsilsesquioxane

Our first objective was to define the pyrolysis characteristics of the methylsilsesquioxane, $\text{-}[MeSi(O)_{1.5}]_x\text{-}$, produced in reaction (3). We have studied the chemical evolution of $\text{-}[MeSi(O)_{1.5}]_x\text{-}$ during pyrolysis from 25°C to 1000°C by chemical analysis and diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). A good portion of this work will be reported at a later date; however, the DRIFTS data shown in Figure 1 are pertinent to the present work. The most useful absorption bands are those that correspond to v O-H (3250-3600 cm^{-1}), v C-H (2750-3000 cm^{-1}) and v Si-H (2100-2230 cm^{-1}). The starting polymer has no bands attributable to an O-H stretching frequency, as expected, given that reaction (3) does not involve hydrolysis.

Insert Figure 1

As the polymer is heated from 25-600°C, very little change is observed in the shapes of these peaks; however, the Si-H bonds diminish with increasing temperature. By 600°C, the peak corresponding to n Si-H disappears and some broadening of the C-H peak is observed as the polymer undergoes extensive crosslinking which "freezes" individual polymer chain segments in

multiple conformations. What is extremely intriguing is that as the polymer is heated to 800°C, Si-H peaks reappear at 2200 and 2250 cm^{-1}. Coincident with the reappearance of Si-H bonds, we also see the formation of a broad peak corresponding to n O-H. This was verified by exchange with D_2O, which shifts a good portion of the O-H stretching vibrations to 2400 cm^{-1} (n O-D).

The disappearance of Si-H bonds in the 600°C intermediate suggests that this material contains only Si-O, Si-C, C-H, and possibly Si-Si bonds. Therefore, we must conclude that the reappearance of Si-H bonds and the appearence of O-H bonds in the 800°C intermediate results as a consequence of the reaction of C-H bonds with Si-O bonds. We assume that Si-C bonds are formed coincident with the formation of the Si-H and O-H bonds. This then is evidence for the first chemical steps in the carbothermal reduction of silica by hydrocarbons. In addition, it also partially delineates the reaction pathway(s) whereby SiC is formed during the pyrolysis of -[MeSi(O)$_{1.5}$]$_x$-. Of primary importance is the fact that we have a partial picture of the decomposition pattern of the -[MeSi(O)$_{1.5}$]$_x$- polymer for use in characterizing the decomposition patterns of any potential copolymer.

SiMe Polysilazane

A number of researchers[2, 7,10] have previously shown that pyrolysis of the SiMe polysilazane, -[MeHSiNH]$_x$-, leads to the formation (at 900°C in N_2) of mixtures of silicon nitride, silicon carbide, and carbon. Typical DRIFTS spectra are shown in Figure 2[10]. Unlike the DRIFTS studies of the -[MeSi(O)$_{1.5}$]$_x$- pyrolytic intermediates, the SiMe intermediates do not exhibit any noteworthy chemical changes apart from the typical broadening of the n N-H and n C-H peaks as the polymer becomes progressively more crosslinked (200-400°C), chars (400-600°C), and eventually becomes a true ceramic material(>600°C). One difference between the SiMe spectra and the SiO spectra is that the n Si-H peaks diminish but never really disappear even at 800°C.

Insert Figure 2

Based on the spectra shown in Figures 1 and 2, it is not clear that we can use DRIFTS as the sole analytical tool with which to follow the chemical evolution of physical mixtures of the two preceramics or true copolymers. Furthermore, studies[11,12] on the pyrolysis of polymers of the general type, -[Me(NH)$_{0.5}$SiO]$_x$- under N_2 and especially NH_3, show that the major product formed is silicon oxynitride (Si_2ON_2). Thus, it is quite possible that Si_2ON_2 will be one of the products formed upon pyrolysis of mixtures of the two preceramics.

However, our initial objectives are: (1) to establish whether or not it is feasible to form copolymers from the two precursors we have chosen to study and; (2) to determine whether or not we can obtain defined microstructures from physical mixtures or copolymers of two inorganic polymers. Furthermore, even if these precursors do eventually produce silicon oxynitride upon

pyrolysis, we are interested in following the kinetics of formation as a function of temperature especially from segregated phases.

With this in mind, we sought to establish the reactivity of the SiMe polysilazane with Cp_2TiMe_2. After repeated tries, we were unable to obtain any type of catalysis. Thus, we assumed that the addition of catalytic amounts of Cp_2TiMe_2 to well-stirred physical mixtures of the SiMe polysilazane ($M_n \approx$ 500-600 D) and -[MeHSiO]$_x$- ($M_n \approx$ 2000 D) would cause only the latter to polymerize. We also assumed that the TGA of a mixture of equivalent amounts of -[MeHSiNH]$_x$- and -[MeHSiO]$_x$- would give an average ceramic yield for the two polymers.

Figure 3 shows the TGA data for pure -[MeHSiNH]$_x$-, -[MeSi(O)$_{1.5}$]$_x$-, and a 1:1 molar mixture of -[MeHSiNH]$_x$- and -[MeHSiO]$_x$- treated with Cp_2TiMe_2. The 900°C ceramic yield for pure -[MeHSiNH]$_x$- is 37% as expected for this molecular weight[9]. The 900°C ceramic yield for -[MeSi(O)$_{1.5}$]$_x$-, produced by Cp_2TiMe_2 catalyzed polymerization of -[MeHSiO]$_x$-, averages about 76-80%. The numerical average expected from a 1:1 equimolar mixture of the two would be 56-58%. As seen in Figure 3, the catalytically transformed 1:1 equimolar mixture gives a polymer with a ceramic yield of approximately 74-76%, which is contrary to what is expected. In fact, it suggests that in the presence of the siloxane, the catalyst is now able to polymerize the polysilazane. To test this possibility and to determine whether or not we could make a range of copolymeric mixtures, we attempted to copolymerize various ratios of -[MeHSiNH]$_x$- (SiMe) to -[MeHSiO]$_x$- (SiO).

Insert Figure 3

Table 1 records the ceramic yields for 1:1, 3:1, 9:1 and 19:1 molar ratios of SiMe to SiO. These yields all differ from the ceramic yield of pure SiMe polysilazane. We conclude that we have found an approach to polymerizing the SiMe alone. One simply needs a certain amount of the hydridosiloxane, which probably generates the active ligand/catalyst. We are currently attempting to determine the lower limit of hydridosiloxane required to generate the true active SiMe polymerization catalyst and to independently synthesize the catalyst.

Given that SiMe is the major component in all but the 1:1 version, these results indicate that we can successfully copolymerize the two preceramics. Tables 1 and 2 list the apparent ceramic compositions following pyrolysis of the preceramics to 900°C in N_2. The apparent ceramic compositions reported in Table 1 are based on the assumption that pyrolysis of the copolymers leads to the formation of the ceramic products normally found for the individual preceramics. Table 2 lists apparent ceramic compositions that are calculated on the assumption that silicon oxynitride is formed as the major ceramic product.

SiMe:SiO	Ceramic Yield (wt %)	Si3N4	SiC	SiO2	C
0:1	78	--	19	70	10
1:0	37	65	24	--	i0
1:1	72	31.3	19.7	38.2	10.4
3:1	62	43.1	19.8	26.7	9.9
9:1	61	52.8	22.1	14.2	10.1
19:1	61	62.0	19.4	7.3	10.7

Table 1. Apparent Ceramic Compositions for Copolymers of SiMe and SiO Assuming That Si_2ON_2 Does Not Form. Apparent compositions based on silicon as the limiting element. Precursors pyrolyzed to 900°C in N_2.

SiMe:SiO	Si2ON2	Si3N4	SiC	SiO2	C
1:1	44.7	0.0	19.7	24.8	10.4
3:1	61.6	0.0	19.9	8.2	9.9
9:1	47.5	19.6	22.1	0.0	10.1
19:1	24.3	45.0	19.4	0.0	10.7

Table 2. Apparent Ceramic Compositions for Copolymers of SiMe and SiO Assuming That Si_2ON_2 Forms. Apparent compositions based on silicon as the limiting element. Precursors pyrolyzed to 900°C in N_2.

Because the 900°C ceramic products we obtain for the SiMe/SiO preceramic mixtures are amorphous, it has not been possible to use x-ray powder diffractometry to determine whether their apparent ceramic compositions are best represented by those listed in Table 1 or Table 2.

Furthermore, heating to higher temperatures, to obtain crystallization, will surely lead to formation of Si_2ON_2; therefore, use of this characterization method would be invalid.

The DRIFTS spectra for the 1:1 mixture, Figure 4, offer some insight into what is probably occuring in the polymerized species. Comparison with the spectra in Figures 1 and 2 shows some

Insert Figure 4

substantial differences especially at the 600 to 800°C range. There is one especially large peak at approximately $1780\ cm^{-1}$. We submit that this may be an amido n C=O peak; however, it is too early to tell. We believe that the set of spectra shown in Figure 4 are distinctly different from an overlay of the spectra found in Figures 1 and 2; therefore, we suspect that segregation is not maintained even at temperatures as low as 600°C and the copolymer system is likely to be a useful precursor to Si_2ON_2 but is probably not a useful model of a block or graft copolymer.

One important observation made in these studies is that under some conditions it is possible to use a titanium based catalyst to polymerize the SiMe polysilazane at room temperature. We are pursuing this system as an alternative to the ruthenium based catalysts we have used until recently[7].

3. Acknowledgements

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Captions for Figures

Figure 1. DRIFT Spectra for Samples of -[MeSi(O)$_{1.5}$]$_x$- Pyrolyzed Under N$_2$ to Various Temperatures. Precursor prepared by reaction of -[MeHSiO]$_x$- (M$_n$ ≈ 2000 D) with Cp$_2$TiMe$_2$, 0.1 wt percent catalyst at room temperature.

Figure 2. DRIFT Spectra for Samples of -[MeHSiNH]$_x$- Pyrolyzed Under N$_2$ to Various Temperatures. Precursor prepared by reaction of -[MeHSiNH]$_x$- (M$_n$ ≈ 600 D) with Ru$_3$(CO)$_{12}$, 0.1 wt percent catalyst at 40°C for 48 h.

Figure 3. Thermogravimetric Analysis of -[MeSi(O)$_{1.5}$]$_x$- (a), -[MeHSiNH]$_x$- (c) and a 1:1 Copolymer of -[MeHSiNH]$_x$- and -[MeSi(O)$_{1.5}$]$_x$- (b). Pyrolyzed Under N$_2$ at a Heating Rate of 5°C/min. SiO precursor and SiMe/SiO copolymer precursor prepared by reaction of -[MeHSiO]$_x$- or a -[MeHSiO]$_x$-/-[MeHSiNH]$_x$- mixture with Cp$_2$TiMe$_2$, 0.1 wt percent catalyst at room temperature.

Figure 4. DRIFT Spectra for Samples of SiMe/SiO Copolymer Precursor Pyrolyzed Under N$_2$ to Various Temperatures. Precursor prepared by reaction of a 1:1 equimolar -[MeHSiO]$_x$-/-[MeHSiNH]$_x$- mixture with Cp$_2$TiMe$_2$, 0.1 wt percent catalyst at room temperature.

Transition Metal Catalyzed Synthesis of Organometallic Polymers

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Abstract: Transition metal catalysts have recently been used to synthesize organo- metallic oligomers and polymers containing boron or silicon in the polymer backbone. Three types of transition metal catalyzed reactions have proven useful for organometallic polymer synthesis: (1) dehydrocoupling by self- reaction ($2E\text{-}H \longrightarrow H_2 + E\text{-}E$) or by reaction with an acidic hydrogen ($E\text{-}H + X\text{-}H \longrightarrow H_2 + E\text{-}X$); (2) redistribution of Si-H bonds with Si-O bonds, $\text{-}[MeHSiO]_x \longrightarrow MeSiH_3 + \text{-}[Me(O)_{1.5}]_x\text{-}$ and, (3) ring opening polymerization. In this review, we examine the potential utility of these catalytic methods for the synthesis of organometallic polymers. In each instance, an effort is made to illustrate the generality or lack thereof for reaction types. Relevant literature and proposed reaction mechanisms for each reaction are discussed.

Introduction

The literature contains tens of thousands of publications and patents devoted to the synthesis, characterization and processing of polymers. Despite the fact that there are more than one hundred elements, the majority of these publications and patents concern polymers with carbon backbones. Furthermore, the limited (by comparison) number of publications on polymers that contain elements other than carbon in their backbones are typically devoted to polymers based on silicon, especially those with Si-O bonds.

This disparity is partially a consequence of the dearth of low cost organometallic feedstock chemicals potentially useful for polymer synthesis. It also derives from the lack of general synthetic techniques for the preparation of organometallic polymers. That is, by comparison with the numerous synthetic strategies available for the preparation of organic polymers, there are few such strategies available for synthesizing tractable, organometallic polymers.

In recent years, commerical and military performance requirements have begun to challenge the performance limits of organic polymers. As such, researchers have turned to organometallic polymers as a possible means of exceeding these limits for a wide range of applications that include: (1) microelectronics processing (e.g. photoresists) [1]; (2) light weight batteries (conductors and semi-conductors) [2]; (3) non-linear optical devices [3] and, (4) high temperature structural materials (e.g. ceramic fiber processing) [4,5].

These requirements also challenge the organometallic chemist to develop new, general synthetic

techniques for the preparation of organometallic polymers. Unfortunately, preparative methods that have proved exceptionally useful for synthesizing organic polymers are frequently useless or unacceptable when applied to organometallic polymer syntheses. For example, the catalytic synthesis of polyolefins occupies a very large niche in organic polymer synthesis; however, these reactions require element-element double bonds in the feedstock chemicals. Element-element double bonds are relatively rare and difficult to synthesize in organometallic compounds. Consequently, this avenue for the catalytic synthesis of organometallic polymers is not viable.

It is well recognized that the only commercially successful polymers, polysiloxanes and polyphosphazenes, are synthesized by ring-opening polymerization, a process which has analogy in organic chemistry. However, it is our opinion that new, general synthetic routes to organometallic polymers will arise from chemistries with limited or without analogy in organic chemistry. In this review article, we explore the potential utility of catalytic methods of synthesizing organometallic polymers. In particular, we will focus on transition metal catalyzed dehydrocoupling reactions, redistribution reactions and ring-opening reactions. In each instance, we will illustrate the generality of a particular reaction, discuss the literature and the proposed reaction mechanisms.

Dehydrocoupling Reactions

Dehydrocoupling reactions, as illustrated by reactions (1) and (2), offer great utility for the synthesis of organometallic polymers because H_2 is generated coincident with product. H_2 is easily

$$2E\text{-}H \xrightarrow{\quad\text{catalyst}\quad} H_2 + E\text{-}E \tag{1}$$

$$E\text{-}H + X\text{-}H \xrightarrow{\quad\text{catalyst}\quad} H_2 + E\text{-}X \tag{2}$$
$$E = \text{Element}, X = O, N, S, E \text{ etc}$$

removed and permits one to drive a thermodynamically unfavorable reaction. Because purification procedures are minimal, the risk of contaminating a reactive and/or thermodynamically unstable polymer is minimized. If the catalyst exhibits sufficiently high activity, then its contribution to the impurity level is also minimized.
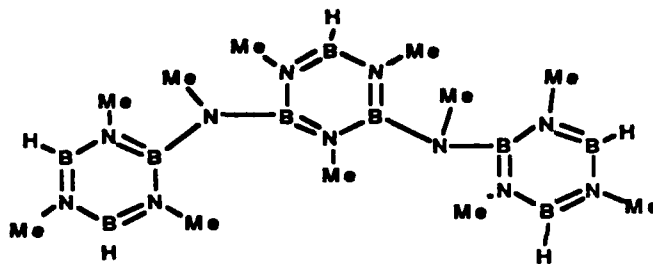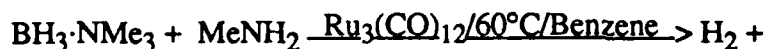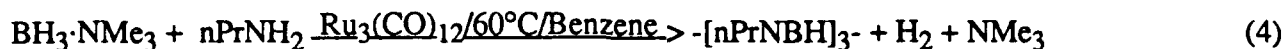
Dehydrocoupling at Boron

Transition metal catalyzed dehydrocoupling polymerization has only been observed for boron and silicon compounds. One of the earliest reports of catalytic dehydrocoupling is that Corcoran and Sneddon [6] on the catalytic dehydrocoupling of boron hydrides and carboranes, e.g. reaction (3) below. Reaction (3) is the only true instance wherein a catalyst has been used to couple B-H bonds to form H_2 and a B-B bond. Unfortunately, this reaction is extremely slow, $\leq$1-2 turnovers/day/mol cat even at catalyst

$$2 \ B_5H_9 \xrightarrow[25°C]{PtBr_2} \ B_{10}H_{16} + H_2 \quad (3)$$
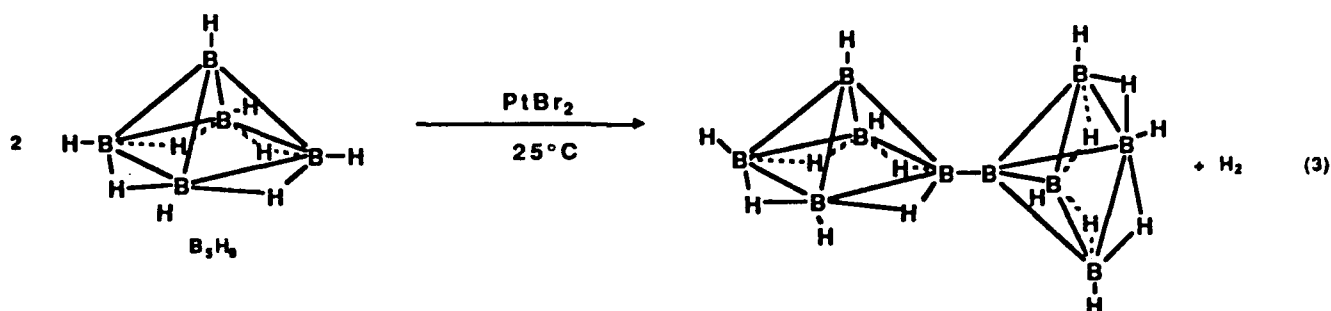
concentrations of 10-20 mole percent of the borane reactants. Reaction rates do not improve at higher temperatures and the reaction does not lead to true polymeric species. However, recent studies with different B-H containing systems have proven more successful.

Thus, a patent by Blum and Laine [7] briefly describes ruthenium catalyzed dehydrocoupling of N-H bonds with B-H bonds to form H_2 and B-N bonds. Two reactions discussed in the patent are:

$$BH_3 \cdot NMe_3 + nPrNH_2 \xrightarrow{Ru_3(CO)_{12}/60°C/Benzene} \ -[nPrNBH]_3 - + H_2 + NMe_3 \quad (4)$$

$$BH_3 \cdot NMe_3 + MeNH_2 \xrightarrow{Ru_3(CO)_{12}/60°C/Benzene} \ H_2 +$$

(5)

Catalyst quantities are normally 0.1 mole percent of the borane complex. In the absence of catalyst, reaction (4) gives only the NMe_3 displacement product, $BH_3 \cdot NH_2 nPr$. In reaction (5), an oily oligomeric material is recovered in approximately 40% yield. Elemental and mass spectral analyses suggest that the product is the trimeric species shown; however, these results require further clarification.

More recently, Lynch and Sneddon [8,9] have begun to study reactions related to reaction (5) using borazine as substrate and $PtBr_2$, $RhCl(PPh_3)_3$ or Harrod's catalyst, dimethyl titanocene (h^5-Cp_2TiMe_2) as catalysts. These catalysts produce dimers and oligomers by B-H/N-H dehydrocoupling. In some instances fairly high molecular weights are obtained. Although complete characterization of the latter materials is not currently available, these polymers appear to be partially crosslinked [reaction (6)], as the BN:H ratio is ca. 3: 3.8 rather than 3:4 as expected for simple stepwise polymerization.

$$\text{(6)}$$
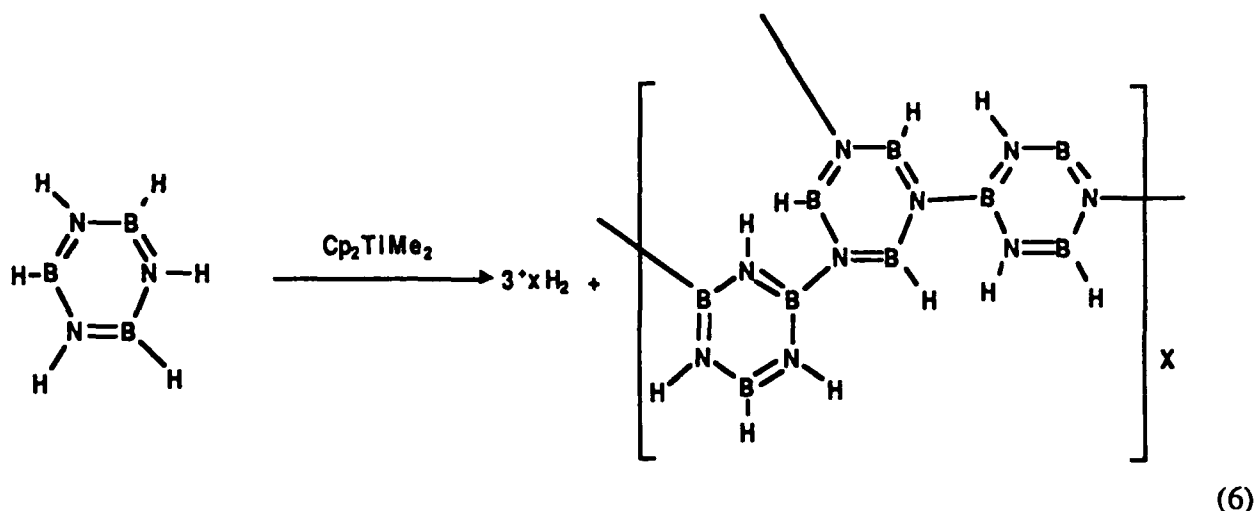
Corcoran and Sneddon [6] propose a tentative mechanism for $PtBr_2$ catalyzed coupling of B-H bonds as illustrated in Scheme 1:

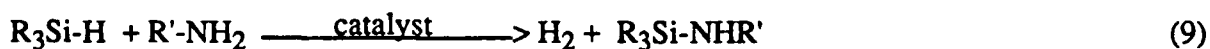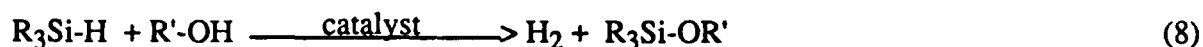$$Pt^{II}HBr + HBr \longrightarrow H_2 + PtBr_2$$
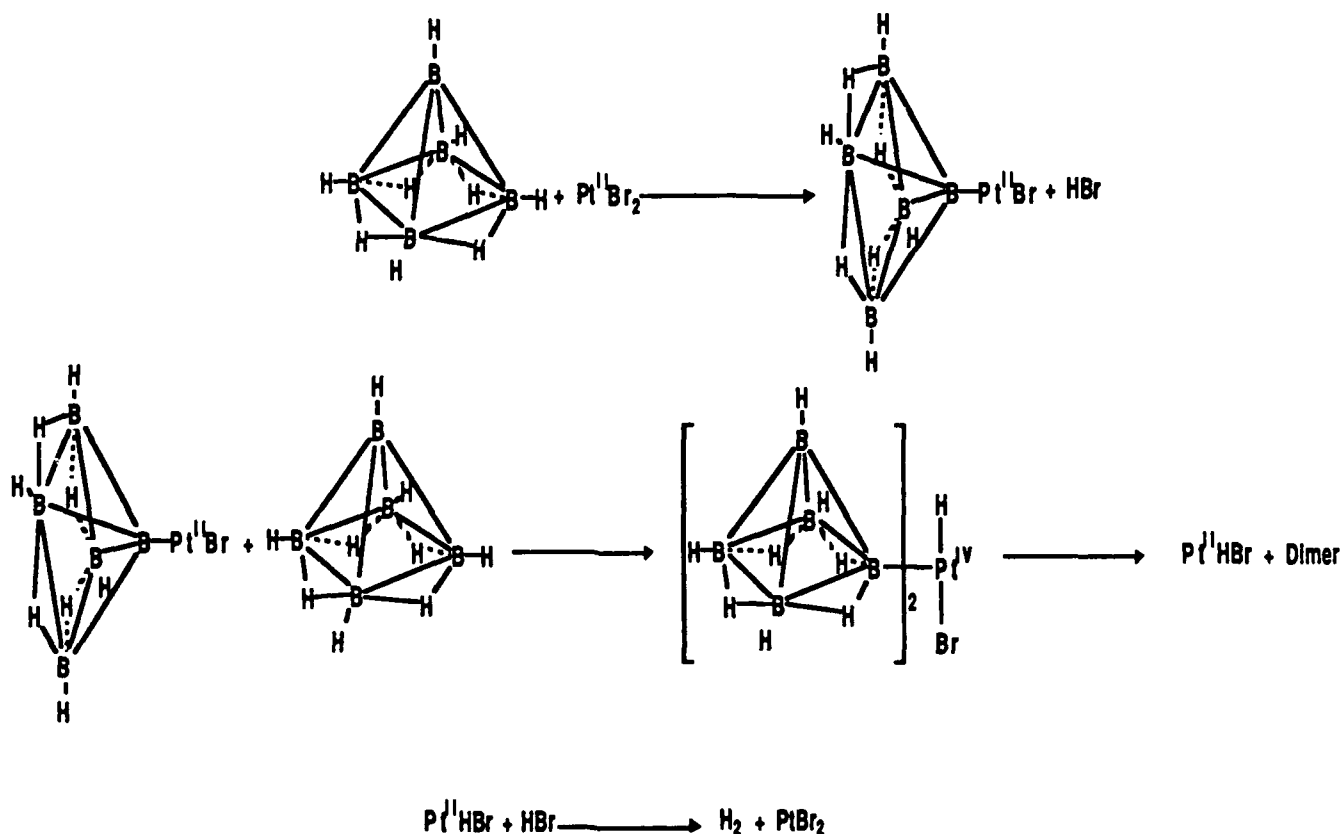
Scheme 1.

If the apical site is blocked with a methyl group, electrophilic substitution does not occur. This, coupled with the exclusive formation of the $1:2'\text{-}[B_5H_8]_2$ isomer, is consistent with a mechanism where oxidative addition occurs only at a basal site. These results are also consistent with earlier work on transition metal catalyzed hydroboration of alkynes using B_5H_9, where evidence also suggests that only

4

basal B-H bonds are catalytically active [10].

The results illustrated by reactions (4) and (5) are preliminary and no efforts have been made to establish reaction mechanisms. The same holds true for titanocene catalysis of reaction (6). However, the following discussions on dehydrocoupling mechanisms in silicon systems, by ruthenium and titanium catalysts, most likely are relevant to dehydrocoupling as it occurs at B-H bonds.

Dehydrocouping at Silicon

The most well studied dehydrocoupling reactions are those involving Si-H bonds. Si-H dehydrocoupling can take two forms; self-reaction and reaction with acidic E-H bonds:

$$2R_3Si\text{-}H \xrightarrow{\quad catalyst \quad} H_2 + R_3Si\text{-}SiR_3 \tag{7}$$

$$R_3Si\text{-}H + R'\text{-}OH \xrightarrow{\quad catalyst \quad} H_2 + R_3Si\text{-}OR' \tag{8}$$

$$R_3Si\text{-}H + R'\text{-}NH_2 \xrightarrow{\quad catalyst \quad} H_2 + R_3Si\text{-}NHR' \tag{9}$$

Both group 8 and early transition metals catalyzed Si-H dehydrocoupling. However, the mechanisms appear to be quite different in the two cases. The following discussions are divided along these lines.

Si-H Self-Reaction Dehydrocoupling

The earliest report of group 8 metal catalyzed self-reaction is that of Ojima et al [11], who describe the redistribution, dimerization and trimerization of simple silanes (Et_2SiH_2, $PhMeSiH_2$ and Ph_2SiH_2) in the presence of Wilkinson's catalyst, $(Ph_3P)_3RhCl$:

$$R_2SiH_2 \xrightarrow{(Ph_3P)_3RhCl/70°C} H_2 + H\text{-}[R_2Si]_n\text{-}H \quad n = 2 \text{ or } 3 \tag{10}$$

Corey et al [12] have recently assessed reaction (10)'s synthetic utility (where $R_2SiH_2 = Ph_2SiH_2$, 9,10-dihydro-9-silaanthracene, silafluorene or dihydrodibenzosilepin) by examining the effects of variations in the reaction conditions on the rates and yields of products. Their findings indicate that low

$$\tag{11}$$
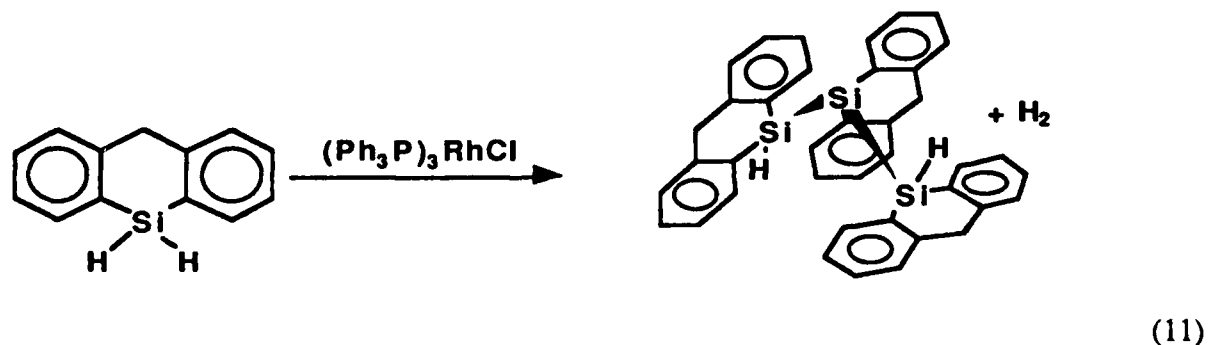
catalyst concentrations and higher temperatures favor the formation of trimer, reaction (11). The standard reaction uses toluene as solvent, 0.25 mole percent catalyst and reaction temperatures of 20-80°C for 1-48 h. Higher reaction temperatures require less reaction time.
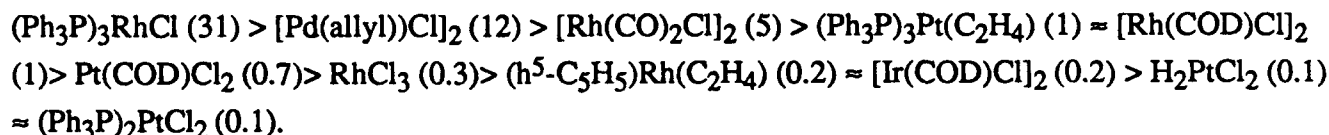
Under identical conditions, the order of reactivities (percent conversion to products) is:

silafluorene (100)> silaanthracene (83)> Ph_2SiH_2 (59) > dibenzosilepin (10)
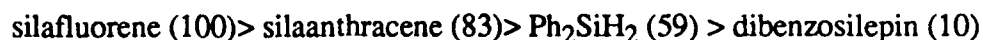
In a complementary study, Brown-Wensley surveyed the ablity of several group 8 metal catalyst precursors to promote dehydrocoupling of Et_2SiH_2 [13]:

$$Et_2SiH_2 \xrightarrow{\quad catalyst/RT \quad} H_2 + HEt_2Si\text{-}SiEt_2H \qquad (12)$$
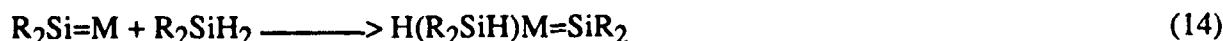
Typical reaction conditions were 1 mole percent catalyst run in neat Et_2SiH_2 for periods of up to 75 h. The following relative activities were observed:
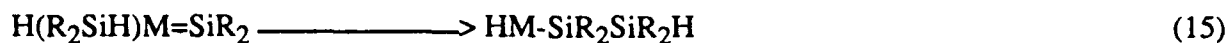
$(Ph_3P)_3RhCl$ (31) > $[Pd(allyl))Cl]_2$ (12) > $[Rh(CO)_2Cl]_2$ (5) > $(Ph_3P)_3Pt(C_2H_4)$ (1) ≈ $[Rh(COD)Cl]_2$ (1)> $Pt(COD)Cl_2$ (0.7)> $RhCl_3$ (0.3)> $(h^5\text{-}C_5H_5)Rh(C_2H_4)$ (0.2) ≈ $[Ir(COD)Cl]_2$ (0.2) > H_2PtCl_2 (0.1) ≈ $(Ph_3P)_2PtCl_2$ (0.1).

Although some of the catalysts: $Pt(COD)Cl_2$, $[Pd(allyl))Cl]_2$, $[Ir(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$, were observed to dehydrocouple Et_3SiH to $Et_3Si\text{-}SiEt_3$, there was no indication that these same catalysts were able to couple $HEt_2Si\text{-}SiEt_2H$. The hydrosilylation activities of this same set of catalysts gave much the same ordering as their dehydrocoupling activities which suggests that similar initial mechanistic steps are involved in both reactions.

Despite the work of Ojima et al [11], Corey et al [12], Brown-Wensley [13], the work of Woo and Tilley [14] on catalytic dehydrocoupling with early transition metals and, the extensive work of Curtis and Epstein [15] on related chemistry, there is no concensus as to a particular mechanism for group 8 metal catalyzed self-reaction dehydrocoupling.

Ojima et al suggested a catalytic cycle, recently expanded by Woo and Tilley, that involves formation of a metal-silylene intermediate generated by a-abstraction:

$$R_2SiH_2 + M \longrightarrow R_2SiH\text{-}M\text{-}H \qquad (12)$$

$$R_2SiH\text{-}M\text{-}H \longrightarrow H_2 + R_2Si{=}M \qquad (13)$$

$$R_2Si{=}M + R_2SiH_2 \longrightarrow H(R_2SiH)M{=}SiR_2 \qquad (14)$$

$$H(R_2SiH)M=SiR_2 \xrightarrow{\hspace{2cm}} HM\text{-}SiR_2SiR_2H \tag{15}$$

or

$$R_2Si=M + R_2SiH_2 \xrightarrow{\hspace{2cm}} HMSiR_2SiR_2H \tag{16}$$

$$HM\text{-}SiR_2SiR_2H \xrightarrow{\hspace{2cm}} M + HSiR_2SiR_2H \tag{17}$$

We suggest that reactions (18) and (19) may also be operative for group 8 metal catalyzed

$$R_2Si=M + R_2SiH_2 \xrightarrow{\hspace{2cm}} R_2HSi\text{-}M\text{-}SiHR_2 \tag{18}$$

$$R_2HSi\text{-}M\text{-}SiHR_2 \xrightarrow{\hspace{2cm}} M + R_2SiH\text{-}SiHR_2 \tag{19}$$
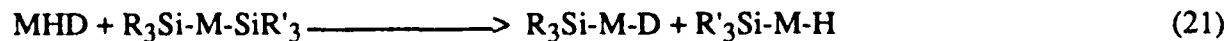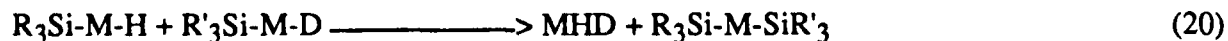
dehydrocoupling as discussed below.

The possible participation of a metal-silylene intermediate in the catalytic formation of polysilanes is supported by Zybill et al's report [16] that the HMPT stabilized iron-silylene complex, $(CO)_4Fe=SiMe_2$, decomposes readily to polysilanes and $Fe_3(CO)_{12}$. However, Curtis and Epstein argue that it is not necessary to invoke silylene intermediates to obtain plausible explanations for the reactions observed. In fact, silylene intermediates cannot form in the catalytic cycle leading to Et_3Si-H dehydrocoupling.

If the catalytic cycle follows reactions (12)-(15) and (17), then the complete catalytic cycle would require the metal center to undergo two consecutive oxidative additions and then two consecutive reductive eliminations for a change of four electrons in each direction. Formally, the metal-silylene is formed by oxidative addition of Si-H to the metal followed by a-abstraction. Reaction (14) requires a second oxidative addition. Because it is unlikely that such a catalytic cycle would be observed for all of the metals found capable of promoting dehydrocoupling, it appears that a catalytic cycle involving reactions (16) and (17) and/or (18) and (19) is more reasonable. We believe that the disilyl intermediate shown in reactions (18) and (19) is operative in at least some catalyst systems because it permits us to explain dimerization of R_3SiH without invoking a metal-silylene complex.

Curtis and Epstein note that the nickel triad readily catalyzes H/D exchange at R_3SiH centers. If four electron redox reactions are not operative, then we must consider bimolecular reactions:

$$R_3Si\text{-}M\text{-}H + R'_3Si\text{-}M\text{-}D \xrightarrow{\hspace{2cm}} MHD + R_3Si\text{-}M\text{-}SiR'_3 \tag{20}$$

$$MHD + R_3Si\text{-}M\text{-}SiR'_3 \xrightarrow{\hspace{2cm}} R_3Si\text{-}M\text{-}D + R'_3Si\text{-}M\text{-}H \tag{21}$$

or

$$R_3Si\text{-}M\text{-}H + R'_3Si\text{-}M\text{-}D \xrightarrow{\hspace{2cm}} R_3Si\text{-}D + H\text{-}M\text{-}M\text{-}SiR'_3 \tag{22}$$

$$H\text{-}M\text{-}M\text{-}SiR'_3 \xrightarrow{\hspace{2cm}} 2M + R'_3Si\text{-}H \tag{23}$$

Other possibilities also exist. Clearly, the species $R_3Si\text{-}M\text{-}SiR'_3$ could reductively eliminate dimer coincident with MHD eliminating HD. An alternate mechanistic explanation could center on metal clusters as catalytic intermediates. Proof for these possible mechanisms, in the form of kinetic studies, is currently lacking in the literature.

Unfortunately, the group 8 metals have proved useful only for the synthesis of simple oligosilanes not for polysilanes. However, Harrod et al [17-20] have discovered that early transition metals provide quite active catalysts for the synthesis of oligo- and polysilanes. These catalysts hold much promise for the synthesis of true polysilanes via self-reaction dehydrocoupling. Harrod et al first described the catalytic dehydrocoupling of mono-substituted silanes by dimethyl titanocene, Cp_2TiMe_2 or $(h^5\text{-}C_5H_5)_2TiMe_2$, catalysts in 1985 [17]. Since then, the list of early transition metal catalysts that promote reaction (24) has grown to include; vanadium [18], zirconium [18], and hafnium [14].

$$xRSiH_3 \xrightarrow{\hspace{0.8cm}\text{catalyst}\hspace{0.8cm}} xH_2 + \text{-}[RSiH]_x\text{-} \tag{24}$$
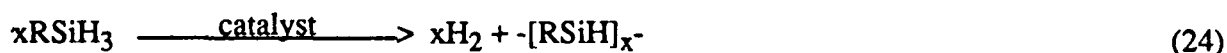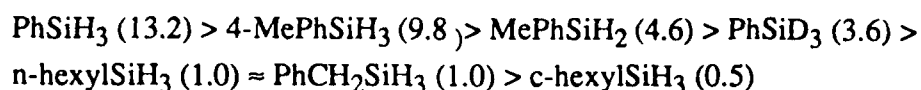
Harrod et al also briefly describe the successful use of thorium and uranium catalysts [18].

The oligomers produced from reaction (24), using dimethyltitanocene as catalyst, are atactic, bimodal and hydrogen terminated [19]. Vapor pressure osmometry indicates that the $PhSiH_3$ and n-hexylSiH$_3$ derived oligomers have molecular weights of 1000-1500 D which corresponds to DPs of about ten and narrow polydispersities. These results are corroborated by size exclusion chromatography studies (GPC) using polystyrene standards. If $(h^5\text{-}C_5H_5)_2ZrMe_2$ is used, DPs of up to 20 silicon units are observed. The bimodel distribution arises because of the production of cyclic species. The all trans-hexaphenyl- cyclohexasilane crystallizes out of solution if the reactions are left to stand.

Titanocene catalyzed polymerization is extremely susceptible to the steric environment about silicon. Furthermore, hydrogen can compete with silane for the catalytically active site on titanium [19]. Thus, efforts to conduct valid kinetic studies and to quantitatively assess the effects of steric environment about silicon on reaction rate and product selectivity required the addition of a sacrificial alkene, reaction (25). If reaction (25) is run with the following set

$$RSiH_3 + R'CH\text{=}CHR' \xrightarrow{Cp_2TiMe_2/toluene/20°C} \text{-}[RSiH]_x\text{-} + R'CH_2CH_2R' \tag{25}$$
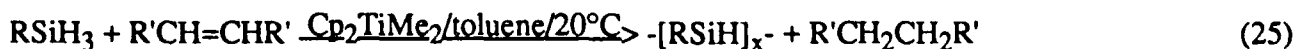
of silanes, under identical conditions, where R'CH=CHR' = cyclohexene, the relative order of reactivities observed is:

PhSiH$_3$ (13.2) > 4-MePhSiH$_3$ (9.8)> MePhSiH$_2$ (4.6) > PhSiD$_3$ (3.6) >
n-hexylSiH$_3$ (1.0) ≈ PhCH$_2$SiH$_3$ (1.0) > c-hexylSiH$_3$ (0.5)

Both c-hexylSiH$_3$ and MePhSiH$_2$ are unreactive except in the presence of the sacrificial alkene. Under the reaction conditions used, both silanes give only dimer products.

MeSiH$_3$ and SiH$_4$ were also studied under the same reaction conditions (toluene solvent, 10 mole percent catalyst). Even without the sacrificial alkene, these silanes were too reactive and difficult to work with. Both silanes tend to give intractable, highly crosslinked polymers. These results are indicative of the severe influence of steric effects at silicon and on the efficacy of the catalytic reaction.

Harrod et al have also examined the reactivity of germanes under the same conditions [20] and find that they are actually more reactive than their silicon counterparts. The only previous effort to couple germanes was that of Marchand et al [21], who find discovered reaction (26):

$$Et_2GeH_2 \xrightarrow{\text{steel wool/75°C}} xH_2 + H\text{-}[Et_2Ge]_x\text{-}H \quad x = 2\text{-}4 \tag{26}$$

Unless care is taken, the monosubstituted germanes also react to give highly crosslinked polymers. Thus, with dimethyltitanocene, PhGeH$_3$ reacts at room temperature to give a gel. However, vanadocene (a poor catalyst for silanes) provides effective stepwise polymerization at 50°C to higher oligomers and polymers that were not further characterized.

Although not useful for monosubstituted germanes, dimethyltitanocene proved to be an effective catalyst for the polymerization of Ph$_2$GeH$_2$, a reaction not possible with the analogous silane. This result is extremely important in defining a mechanism for both the silane and germane the polymerization reactions assuming the mechanisms are the same.
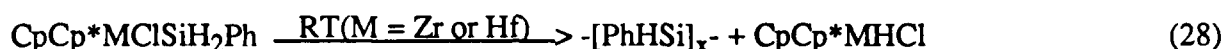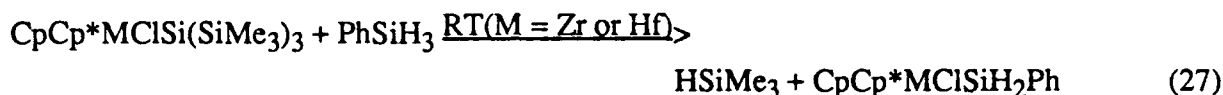
Harrod et al [17-20] and Tilley et al [14,22] have undertaken detailed studies to elucidate the reaction mechanisms whereby early transition metals promote self-reaction dehydrocoupling in an effort to develop better catalysts. The long term goal is to catalytically prepare high molecular weight polysilanes and polygermanes with well defined properties.

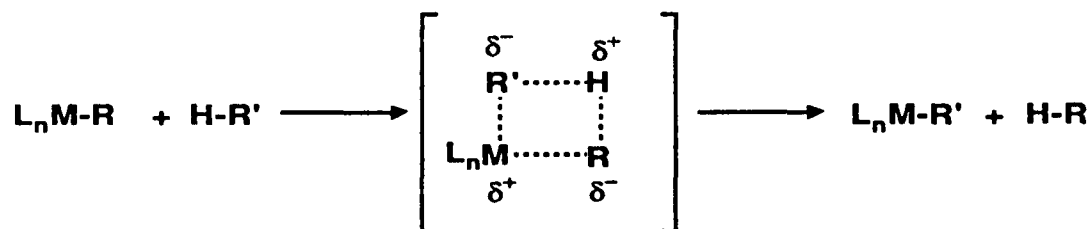Harrod et al have isolated the following complexes from reaction solutions:
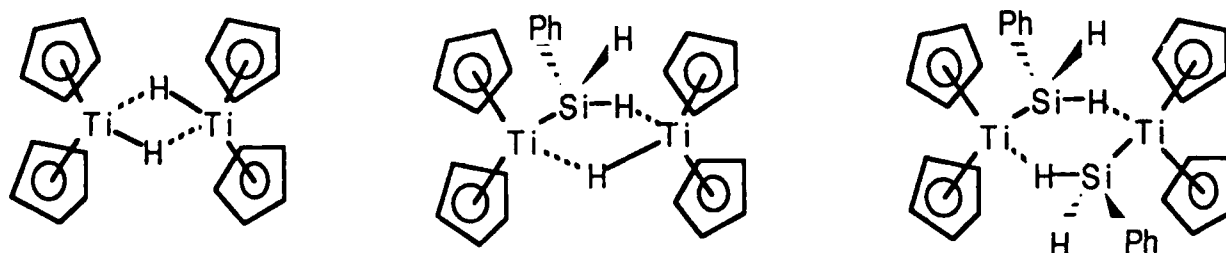
Unfortunately, these complexes do not appear to be true intermediates in the catalytic cycle. Woo

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and Tilley [14;22], in an effort to slow the catalytic reaction down so that intermediates can be isolated, have studied the zirconium and hafnium systems. They find that the $CpCp*ZrClSi(SiMe_3)_3$ and $CpCp*HfClSi(SiMe_3)_3$ (where $Cp* = Me_5Cp$) complexes undergo stoichiometric reactions with $PhSiH_3$, reaction (27). The product of this stoichiometric reaction decomposes, reaction (28), to form $-[PhHSi]_x-$ polymers rather than oligomers:

$$CpCp*MClSi(SiMe_3)_3 + PhSiH_3 \xrightarrow{RT(M = Zr \text{ or } Hf)}$$

$$HSiMe_3 + CpCp*MClSiH_2Ph \qquad (27)$$

$$CpCp*MClSiH_2Ph \xrightarrow{RT(M = Zr \text{ or } Hf)} -[PhHSi]_x- + CpCp*MHCl \qquad (28)$$

Typically, the presence of chloride substituents limits reactions to stoichiometric events or totally inhibits reaction. Thus, $Cp*ZrSi(SiMe_3)_3Cl_2$ is inactive, while both $Cp_2Ti(SiMe_3)Cl$ and $Cp*Ta(SiMe_3)Cl_3$ will only dimerize $PhSiH_3$. In contrast, the complex, $CpCp*Zr(SiMe_3)Si(SiMe_3)_3$, can be used to successfully catalyze the polymerization of $PhSiH_3$ to give much higher molecular weight polymers with DPs of up to 40, coincident with the formation of cyclomers. Likewise, Chang and Corey report that in contrast to titanocene, which will dimerize $MePhSiH_2$ only in the presence of alkene, zirconocene will oligomerize $MePhSiH_2$ to give at least pentasilanes [12b].

The proposed reaction mechanism is unlike that suggested above for the group 8 metal catalysts. It probably requires s-bond metathesis. These are reactions which have four-center transition states:

$$L_nM-R \;+\; H-R' \longrightarrow \begin{bmatrix} \overset{\delta^-}{R'} \cdots\cdots \overset{\delta^+}{H} \\ \vdots \qquad\qquad \vdots \\ \underset{\delta^+}{L_nM} \cdots\cdots \underset{\delta^-}{R} \end{bmatrix} \longrightarrow L_nM-R' \;+\; H-R$$

Reactions (27) and (28) are representative of a s-bond metathesis reaction. The activation parameters for reaction (28) where M = Hf are $\Delta H^{\pm} = 16.4$ kcal/mol, $\Delta S^{\pm} = -27$ eu and $K_H/K_D = 2.5$. The values parallel those found for previously observed s-bond metathesis reactions [23].

If we accept this as the likely mode of reaction, then we must still outline a reasonable catalytic cycle. Kinetic studies of the decomposition of $CpCp*HfClSiH_2Ph$ to $CpCp*MHCl$ and $-[HSiPh]_x-$ reveal a 2nd order rate dependence on $[CpCp*HfClSiH_2Ph]$ with $\Delta H^{\pm} = 19.5$ kcal/mol, $\Delta S^{\pm} = -21$ eu. Woo and Tilley suggest that this indicates a four center transition state and permits them to propose a polymerization reaction such as shown in Scheme 2:
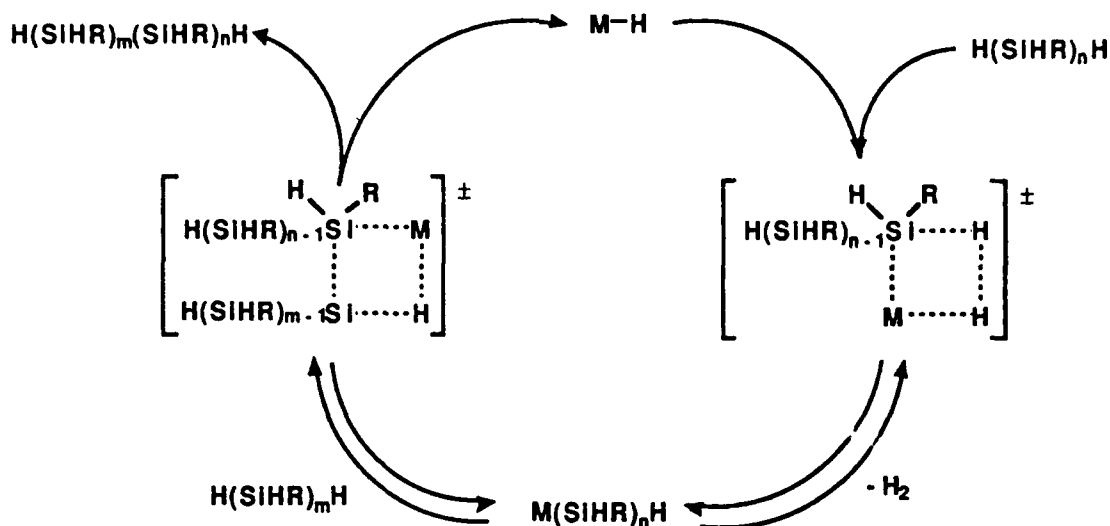
Scheme 2.

Harrod et al have argued [18] that metal-silylene-like intermediates formed by a-abstraction play a role in the early transition metal catalyzed polymerization of silanes; however, their ability to catalyze polymerization of Ph_2GeH_2 [20] provides evidence against this type of intermediate. Woo and Tilley have also explored the possibility that metal-silylene intermediates might play a role in their polymerization studies. However, when reaction (28) is carried out in the presence of silylene traps such as $HSiEt_3$, (c-hexyl)SiH_3, Ph_2SiH_2 or $PhMeSiH_2$, these species exhibit no influence on the course of events. Further support for the mechanism shown in Scheme 2 comes when reaction (28) (where M = Hf) is run with two equivalents of $PhSiH_3$. This reaction leads to the formation of phenylsilane dimers and trimers. With time, a new species appears that is probably the tetramer.

Further work required in the area of polysilane self-reaction dehydrocoupling is likely to focus on optimization of catalyst activity, especially with respect to the synthesis of high molecular weight polymers as there is considerable interest in polymers of this type [1]. In addition, the same driving forces for commercialization of high molecular weight polysilanes should also lead to work on the synthesis of linear polygermanes. An additional area of interest is the development of catalysts that will permit the synthesis of tractable polymethylsilane, -[MeSiH]$_x$-, and polysilane itself, -[H$_2$Si]$_x$-. The former is of interest as a preceramic and the latter would have many useful applications in the electronics industry.
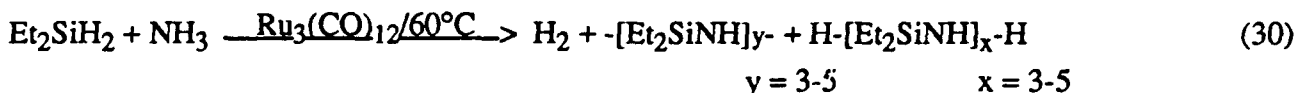
Si-H Catalytic Reactions with E-H

The first reports describing catalytic reaction of Si-H bonds with compounds containing acidic hydrogen were those of Chalk [24] and Corriu et al [25]. These reactions involved the alcoholysis of silanes:

$$ROH + R'_3Si\text{-}H \xrightarrow{\quad catalyst \quad} H_2 + R'_3Si\text{-}OR \qquad (29)$$
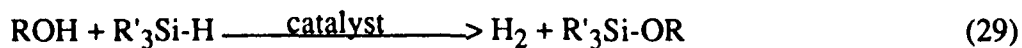
Although these reactions are not useful for the synthesis of organometallic polymers, except perhaps for polysiloxanes (where ROH = H_2O and $R'_3SiH = R'_2SiH_2$), they set the stage for later work wherein the active hydrogen species is an amine [26-30]:

$$RNH_2 + R'_3Si\text{-}H \xrightarrow{\quad catalyst \quad} H_2 + R'_3Si\text{-}NHR \qquad (29)$$
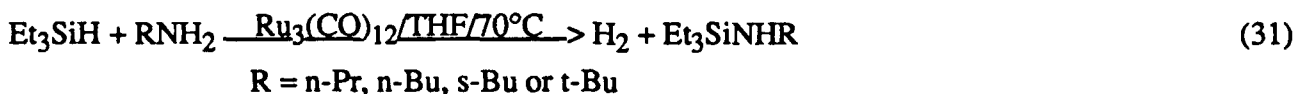
The synthesis of polysilazane oligomers via dehydrocoupling has been studied extensively by Laine et al [29, 31-35], using a variety of amine and silane reactants. For example, if Et_2SiH_2 is reacted with NH_3, reaction (30),

$$Et_2SiH_2 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C} H_2 + \text{-}[Et_2SiNH]_y\text{-} + H\text{-}[Et_2SiNH]_x\text{-}H \qquad (30)$$
$$y = 3\text{-}5 \qquad x = 3\text{-}5$$

then the major products are primarily cyclomers with the cyclotrisilazane
predominating and small quantities of low molecular weight linear oligomers. Typically the catalyst concentration is 0.1 to 0.01 mole percent. Catalyst concentrations at the ppm level can be used for some reactions.

It has not been possible to prepare high molecular weight polysilazanes using reactions analogous to (30) for a variety of reasons. Modeling studies were run using reaction (31), in an effort to find the best conditions for

$$Et_3SiH + RNH_2 \xrightarrow{Ru_3(CO)_{12}/THF/70°C} H_2 + Et_3SiNHR \qquad (31)$$
$$R = n\text{-}Pr, n\text{-}Bu, s\text{-}Bu \text{ or } t\text{-}Bu$$

polymer formation [31].

The kinetics and the catalytic cycle(s) for this reaction are extremely complex. In the absence of amine, the silane reacts with $Ru_3(CO)_{12}$ to produce $(Et_3Si)_2Ru_2(CO)_8$, reaction (32), which can be isolated and used in place of $Ru_3(CO)_{12}$. Catalyst concentration studies demonstrate that the rate of

$$6Et_3SiH + 2Ru_3(CO)_{12} \xrightarrow{110°C/10 \text{ min}} 3H_2 + 3(Et_3Si)_2Ru_2(CO)_8 \qquad (32)$$
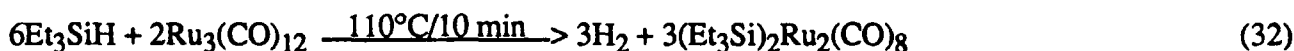
reaction (31) is nonlinearly and inversely dependent on either $[Ru_3(CO)_{12}]$ or $[(Et_3Si)_2Ru_2(CO)_8]$. On a molar basis, $(Et_3Si)_2Ru_2(CO)_8$ is the more active of the two catalyst precursors. These results suggest that the true catalyst forms by cluster fragmentation. Indeed, some evidence was found for the formation of trans-$(Et_3Si)_2Ru(CO)_4$. Thus, higher catalyst concentrations do not improve reaction rates significantly.

A second problem, which also plagues self-reaction dehydrocoupling, is that the reaction rate and

product selectivities are extremely susceptible to the steric environment about both silicon and nitrogen. In rate vs [RNH$_2$] studies, the steric bulk of R controls both the reaction rate and the mechanism. The simple primary amines, n-PrNH$_2$ and n-BuNH$_2$ show an inverse, nonlinear rate dependence on [RNH$_2$] despite the fact that they are reactants.

By comparison, the [s-BuNH$_2$] studies reveal a nonlinear positive rate dependence. On moving to the most bulky amine, t-BuNH$_2$, the rate shows almost no dependence on either [t-BuNH$_2$] or [Et$_3$SiH]. The relative global rates of reaction are n-PrNH$_2$ ≥ n-BuNH$_2$ > s-BuNH$_2$ » t-BuNH$_2$. The potential product, (Et$_3$Si)$_2$NR, corroborated by Kinsley et al [30], is never observed with the ruthenium catalyst.

Apparently, the simple primary amines react with Ru$_3$(CO)$_{12}$ to form fairly stable complexes that deplete the reaction mixture of active catalyst:

$$Ru_3(CO)_{12} + EtCH_2NH_2 \longleftrightarrow (\mu^2\text{-}EtCH=NH)H_2Ru_3(CO)_{10} \qquad (33)$$
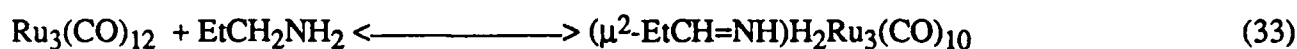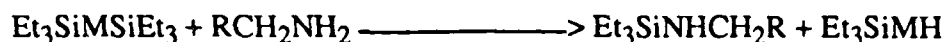
Hence, the inverse dependence on [n-RNH$_2$]. With s-BuNH$_2$, the stability of the amine ruthenium complex is sufficiently reduced such that it plays only a minor role in the catalytic cycle.

With t-BuNH$_2$, there is no a-hydrogen and the amine-ruthenium complex cannot form. However, the fact that the rate is simultaneously independent of both [Et$_3$SiH] and [t-BuNH$_2$], is more difficult to explain and suggests that an alternate mechanism is operative. One can envision a situation in which the rate determining step is catalyst activation; however, *silyl-ruthenium complexes form readily in the absence of amine*. Therefore reaction of the amine at the silicon must be the rate determining step. Crabtree et al have recently studied iridium catalyzed alcoholysis of Et$_3$SiH and proposed that the reaction proceeds via nucleophilic attack of alcohol on a two-electron three-center Si-H⋯M intermediate [36]. Perhaps such an intermediate occurs in this instance. Alternately, the slow step may arise as a consequence of cluster fragmentation. The cluster fragmentation possiblity seems reasonable given that the rate vs [Ru$_3$(CO)$_{12}$] studies with t-BuNH$_2$ reveal first order dependence on catalyst concentration rather than inverse dependence. These combined results suggest a catalytic cycle such as shown in Scheme 3:
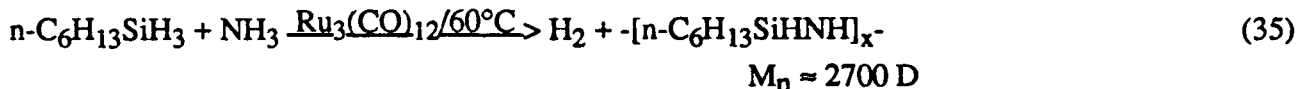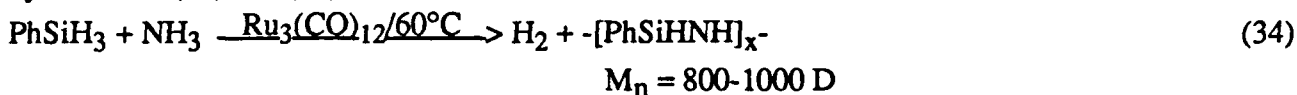
$$M_3 + RCH_2NH_2 \longleftrightarrow H_2(RCH=NH)M_3$$

$$M_3 + 3Et_3SiH \longrightarrow 3HMSiEt_3$$

$$Et_3SiMH + Et_3SiH \longleftrightarrow H_2 + Et_3SiMSiEt_3$$

$$Et_3SiMH + RCH_2NH_2 \longrightarrow Et_3SiNHCH_2R + MH_2$$

and/or

$$\text{Et}_3\text{SiMSiEt}_3 + \text{RCH}_2\text{NH}_2 \longrightarrow \text{Et}_3\text{SiNHCH}_2\text{R} + \text{Et}_3\text{SiMH}$$

$$\text{MH}_2 \longleftarrow\longrightarrow \text{M} + \text{H}_2$$
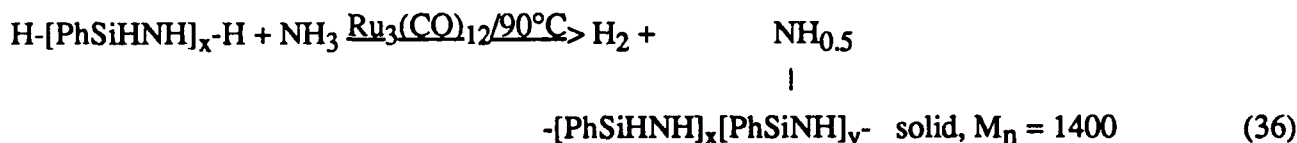
Scheme 3.

The severe steric effects observed in reaction (31) are also observed when the dehydrocoupling reaction is used to synthesize oligosilazanes. Reaction (30) exemplifies these effects. This reaction was an attempt to prepare linear, high molecular weight diethylpolysilazanes. Yet, the only products are mixtures of the cyclotrimer and cyclotetramer with low molecular weight linear species ($M_n \approx 500$ D). In contrast, the use of monosubstituted silane precursors provides access to true oligosilazanes as illustrated by reactions (34) and (35):

$$\text{PhSiH}_3 + \text{NH}_3 \xrightarrow{\text{Ru}_3(\text{CO})_{12}/60°\text{C}} \text{H}_2 + \text{-[PhSiHNH]}_x\text{-} \tag{34}$$
$$M_n = 800\text{-}1000 \text{ D}$$

$$\text{n-C}_6\text{H}_{13}\text{SiH}_3 + \text{NH}_3 \xrightarrow{\text{Ru}_3(\text{CO})_{12}/60°\text{C}} \text{H}_2 + \text{-[n-C}_6\text{H}_{13}\text{SiHNH]}_x\text{-} \tag{35}$$
$$M_n \approx 2700 \text{ D}$$

At 60°C, both oligosilazanes are essentially linear. No evidence is found for dehydrocoupling at the tertiary Si-H bonds or at the internal N-H bonds. At 90°C, the tertiary Si-H bonds react to give partially crosslinked oligosilazanes as shown for the phenylpolysilazane in reaction (36):

$$\text{H-[PhSiHNH]}_x\text{-H} + \text{NH}_3 \xrightarrow{\text{Ru}_3(\text{CO})_{12}/90°\text{C}} \text{H}_2 + \qquad \text{NH}_{0.5}$$
$$\vert$$
$$\text{-[PhSiHNH]}_x\text{[PhSiNH]}_y\text{-} \quad \text{solid, } M_n = 1400 \tag{36}$$

Reactions (34) and (35) can be run at room temperature, if $\text{Ru}_3(\text{CO})_{12}$ is heated (activated Ru Cat) in neat silane prior to addition of NH_3 [35].

In contrast to PhSiH_3 and n-hexylSiH_3, EtSiH_3 reacts indiscriminantly to give a crosslinked polysilazane that is sufficiently intractable to permit effective characterization. The reactivity differences found for PhSiH_3 and n-hexylSiH_3, when compared to EtSiH_3, are quite reminiscent of the reactivity differences found for PhSiH_3 and n-hexylSiH_3 versus MeSiH_3 for self-reaction dehydrocoupling as discussed by Harrod et al [19,20].

The same dehydrocoupling reaction used to synthesize simple oligosilazanes can also be used to further polymerize oligosilazanes produced via other chemical routes. Recent interest in the use of polysilazanes as silicon nitride preceramic polymers [4] originally prompted exploration of dehydrocoupling as a synthetic technique [31-35].

Oligomers of most polysilazanes ceramic precursors have been synthesized by ammonolysis of H_2SiCl_2 or MeSiHCl_2, as in reaction (37):

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$$H_2SiCl_2 + 3MeNH_3 \xrightarrow{\text{0°C/Et}_2\text{O}} HNMe\text{-}[H_2SiNMe]_x\text{-}H + 2MeNH_3Cl \tag{37}$$

Unfortunately, these reactions lead to oligosilazanes with molecular weights too low to have useful polymeric properties. Fortunately, because they contain both Si-H bonds and N-H bonds, ruthenium catalyzed dehydrocoupling can be used to further polymerize these simple olgomers:

$$HNMe\text{-}[H_2SiNMe]_x\text{-}H \xrightarrow{\text{Ru}_3\text{(CO)}_{12}\,/60\text{-}90°C} \text{polymers} \tag{38}$$

When reaction (38) (where $x \approx 20$, $M_n \approx 1200$ D) is run over a 65 h period, M_n increases to only 2300 D with $M_w \approx 25,000$ D. The polysilazane viscosity changes from approximately 1-3 poise to 100 poise in the same time period. These results are typical of a gelation process. However, the GPC curve for the 65 h run [37], indicates that a significant portion of the polymer has a molecular weight well above 10K daltons.

The GPC curve is bimodal which suggests more than one mechanism for polymerization. In recent work, Youngdahl et al [35] find evidence for an additional mechanism for oligosilazane coupling. They find that the amine capped oligosilazanes produced in reaction (37), normally stable to >100°C, will condense in the presence of catalyst, reaction (39):

$$2\text{ --SiNHMe} \xrightarrow{\text{activated Ru Cat/40°C}} MeNH_2 + \text{--Si-N(Me)-Si--} \tag{38}$$
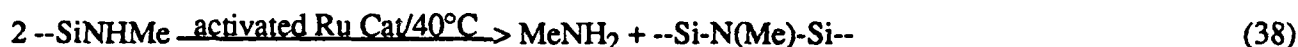
Two other catalytic methods of synthesizing oligo- and polysilazanes have also been discovered as discussed in the following sections.
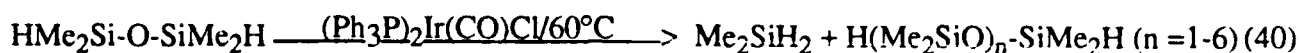
Redistribution Reactions

Redistribution reactions, as defined here, involve the exchange of ligands or moieties between silicon centers, reaction (39):

$$SiX_n + SiY_m \xleftrightarrow{\text{catalyst}} SiX_{n-z}Y_z + SiY_{m-z}X_z \tag{39}$$

The use of n and m in place of 4 allows for the possibility that such catalytic exchanges may occur between penta- or hexacoordinated silicon species in addition to four coordinate silicon compounds.

Transition-metal promoted catalytic redistribution on silicon has already been well reviewed by Curtis and Epstein [15]. Some overlap between the two reviews is necessary given the different objectives; however, the majority of the work discussed below is new. In particular, the interest in this section is on the redistribution reactions of Si-H and Si-O bonds to form silisesquioxane polymers.

Curtis et al [15] have examined the utility of group 8 metal catalyzed redistribution of hydridosiloxanes, tetramethyldisiloxane in particular:

$$HMe_2Si\text{-}O\text{-}SiMe_2H \xrightarrow{\text{(Ph}_3\text{P})_2\text{Ir(CO)Cl/60°C}} Me_2SiH_2 + H(Me_2SiO)_n\text{-}SiMe_2H \quad (n = 1\text{-}6) \quad (40)$$

In addition to Me_2SiH_2 and simple oligomers, the iridium catalyst used in reaction (40) also promotes methyl group transfer to form Me_3Si- capped oligomers. Although higher oligomers are also produced, their concentrations are small. The mechanism has already been discussed in detail and will not be covered here except to note that Curtis and Epstein state that there are discrepancies between what is suggested and the experimental evidence, especially with regard to alkyl transfers. The problem of a four electron redox process, as mentioned above, is also discussed. Further work on reaction (40) is clearly of interest in light of these discrepancies, Luo and Crabtree's results [36], and the possibility of binuclear reactions, as discussed above.

As with group 8 metal catalyzed self-reaction dehydrocoupling, group 8 metal catalyzed redistribution of hydridosiloxanes gives only oligomeric species. If the early transition metals, in particular Harrod's catalyst are used, considerable changes in product distribution are obtained.

Harrod et al [38] first described titanium catalyzed redistribution of simple hydridosiloxanes, e.g. $(EtO)_2MeSiH$ in 1986 and have recently followed up with a more detailed communication on the subject [39]:

$$(EtO)_2MeSiH \xrightarrow{\text{Cp}_2\text{TiMe}_2/\text{RT}} (EtO)_3SiMe + MeSiH_3 \quad (41)$$

This reaction, which can be run neat or in a variety of solvents with less than 0.01 mole percent catalyst, can be used very successfully to form polydi- methylsiloxane polymers from $HMe_2SiOSiMe_2H$, as in reaction (40), with Cp_2TiMe_2 catalyst. The polymers have $M_n \approx 10K$ D and a polydispersity of 1.6. The proton and silicon NMRs are indistinguishable from commercially produced polydimethylsiloxane.

Methysilsesquioxane polymers can also be produced in a similar manner if the reactants contain -[MeHSiO]- groups, reaction (42). The source of the -[MeHSiO]- groups can either be cyclomers or

$$\text{-[MeHSiO]}_x\text{-} \xrightarrow{\text{Cp}_2\text{TiMe}_2/\text{RT/N}_2} MeSiH_3 + \text{-[MeSi(O}_{1.5})]_x\text{-} \quad (42)$$
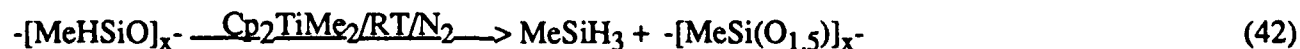
linear oligomers [40]. The titanocene catalyst is heat and light sensitive and, somewhat air sensitive. Reactions such as (42) typically have an induction period which can range from minutes to hours depending on the amount of oxygen present in the system. This induction period appears to be solely for catalyst activation. Once the reaction has started, the initial yellow color of the dimethyl titanocene changes rapidly to royal blue and the reaction is complete in a matter of minutes. No matter what the starting compound, if the reaction is run neat, the final product has a composition that is about -[MeHSiO]$_{0.35}$[MeSi(O$_{1.5}$)]$_{0.65}$-. This polymer, when heated to >200°C, loses all of its -[MeHSiO]- groups to form a polymer consisting entirely of -[MeSi(O$_{1.5}$)]$_x$-, methylsilsesquioxane. The

-[MeSi(O$_{1.5}$)]$_x$- polymer is stable to greater than 500°C in nitrogen [40].

Because of the interest in new routes to polysilazanes, attempts were made to use the Harrod catalyst for redistribution of the silazane, -[MeHSiNH]$_x$- [41]. Unfortunately, the titanocene catalyst is inactive for redistribution when oxygen is replaced by nitrogen; although the solutions do turn blue. What is intriguing about this system is that if dimethyl titanocene is added to mixtures of -[MeHSiO]- and -[MeHSiNH]$_x$-, then polymerization at room temperature does occur. In fact, the MeHSiO : MeHSiNH ratio can be varied from 1:1 to 1:50 without affecting the catalyst's activity. This catalyst system provides a new route to polysilazane polymers.

Harrod et al [39] proposed two mechanisms for reaction (40), Scheme 4 and Scheme 5, that may
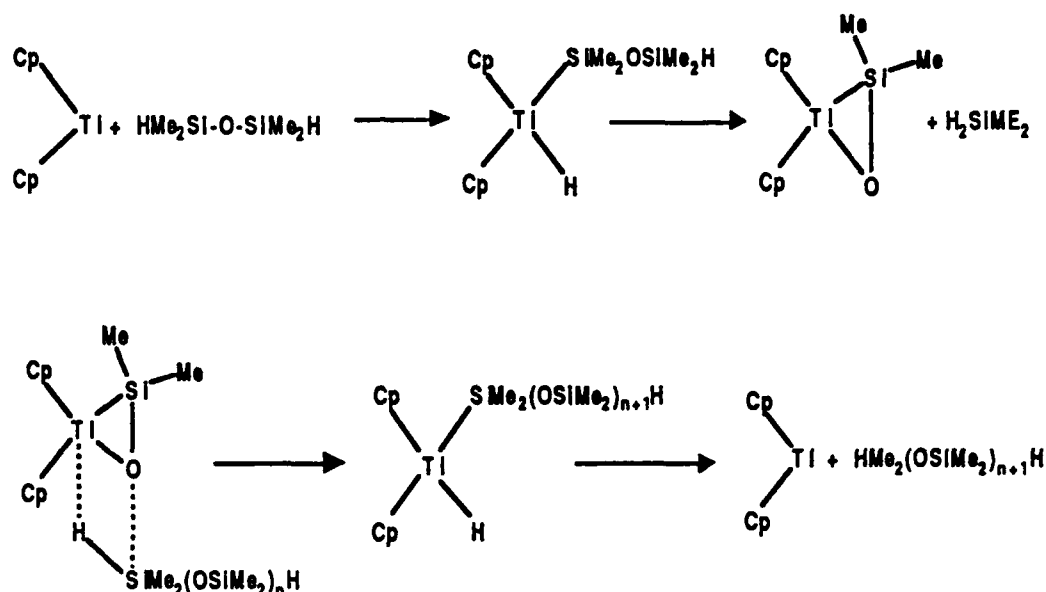
Scheme 4.

explain what occurs during redistribution catalysis. In Scheme 4 the active catalyst is a mononuclear, Ti (IV) complex. In Scheme 5 catalysis requires two Ti (III) metal centers. The authors prefer the Scheme 5 mechanism because all of the species isolated from solution to date (see above) are Ti (III) species:
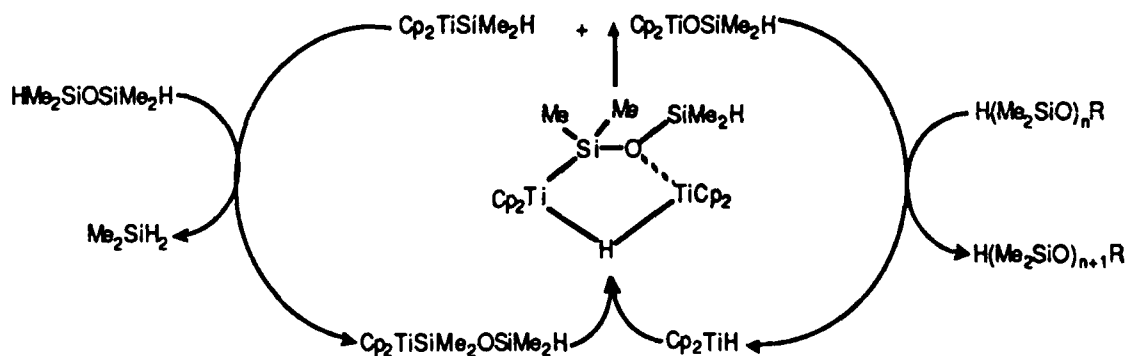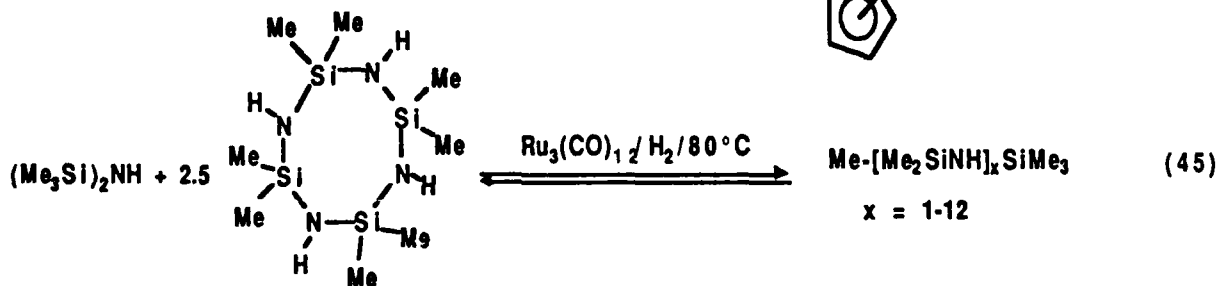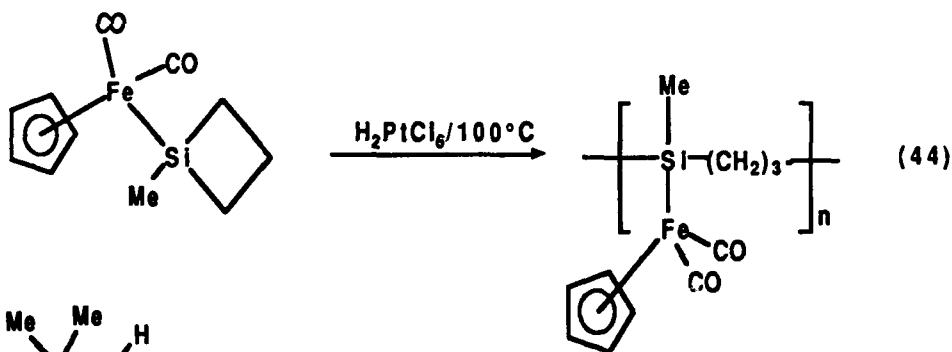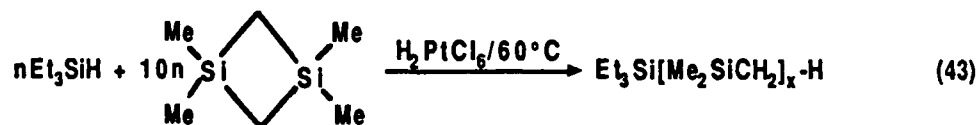

Scheme 5.

Considerably more work needs to be done on these reactions, especially in view of the silazane results, before a detailed understanding of the catalytic cycle is possible. These findings are of significant

commercial interest, because the titanium catalysts offer much higher activity than possible with the group 8 metal catalysts as well as good product selectivity and, entrée to new, potentially useful silsesquioxane polymers.

Ring-Opening Catalysis

Transition metal catalyzed ring opening is the oldest reaction known for the catalytic synthesis of organometallic polymers [42,43]. Again, the only known examples involve heterocyclic monomers that contain silicon, cyclic carbosilanes or silazanes. Ring-opening polymerization of cyclic carbosilanes was discussed by Curtis and Epstein [15]. As such, discussion here is limited primarily to new developments.

Reactions (43)-(45) are examples of transition metal catalyzed ring opening polymerization [34,42-47]. Reaction (43), in the absence of a silane, provides gummy high polymers with molecular weights of 10^5 to 10^6 D. Addition of silane permits the synthesis of lower molecular weight silane capped polymers and oligomers. Reaction (44) is exceedingly interesting

$$nEt_3SiH + 10n \text{ (cyclic)} \xrightarrow{H_2PtCl_6/60^\circ C} Et_3Si[Me_2SiCH_2]_x\text{-H} \qquad (43)$$

$$\xrightarrow{H_2PtCl_6/100^\circ C} \qquad (44)$$

$$(Me_3Si)_2NH + 2.5 \text{ (cyclic)} \xrightleftharpoons{Ru_3(CO)_{12}/H_2/80^\circ C} Me\text{-}[Me_2SiNH]_xSiMe_3 \qquad (45)$$

$$x = 1\text{-}12$$

because it leads to one of the first organometallic polymers containing a pendant organometallic ligand. Reaction (44) gives similar materials although no molecular weights are reported [46]. Reaction (45) can also be run in the absence of capping agent, $(Me_3Si)_2NH$. This leads to higher molecular weight,hydrogen capped oligomers, albeit in much lower yields.

Reactions (43) and (44) are normally run at 50-150°C with less than 1 mole percent catalyst. Most of the group 8 metals will catalyze these reactions; however, platinum compounds afford the best catalyst

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activities.[44]

Although, several mechanisms have been proposed for reactions (43) and (44) [15,44.45]; a mechanism that fits all the facts has not been forthcoming. For example, Cundy et al [45] have suggested a catalytic sequence involving chlorine transfer polymerization; however, many catalysts and cyclic carbosilanes undergo ring opening polymerization in the absence of chlorine. Thus, such a mechanism is not likely to serve as a general model.

Scheme 6 presents a reasonable mechanistic explanation for what has been reported to date; however, it should not be considered definitive:
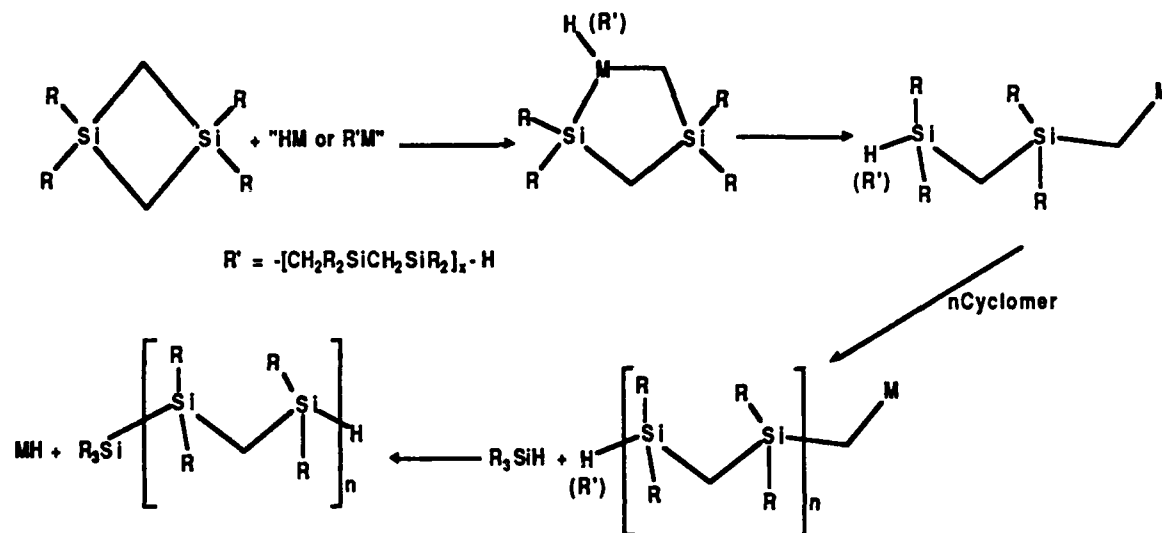
Scheme 6.

The mechanism for catalytic ring opening oligomerization of cyclo- silazanes, reaction (45), as shown in Scheme 7, appears to be similar to that suggested in Scheme 6, for cyclic carbosilanes. In both cases, it is likely
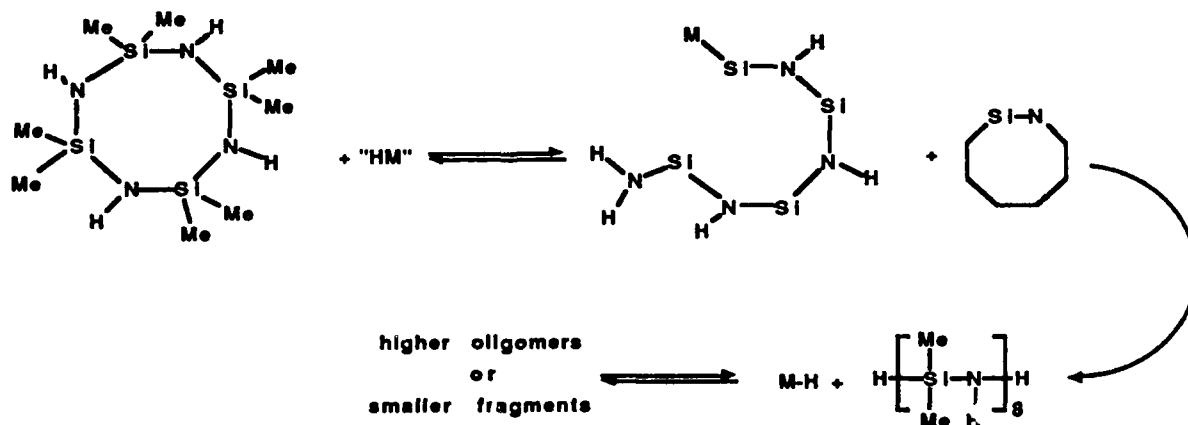
Scheme 7.

that metal hydride are necessary interemediates for effective polymerization.

In fact, the introduction of 1 atm of H_2 to reaction (45), permits equilibration in 1 h at 80°C;

whereas, without H_2, equilibrium is not obtained even after 24 h at 135°C. Furthermore, the $Ru_3(CO)_{12}/H_2$ (1 atm) catalyst system can be replaced with $H_4Ru_4(CO)_{12}$ without affecting reaction rate.

At equilibrium, the 1:2.5 ratio capping agent to cyclotetrasilazane system gives a product mixture that consists of 80% polymers and 20% cyclomers with the trimer predominating. In the absence of capping agent, conversion to linear, hydrogen capped oligomers is reduced to 20% of the total products. However, the molecular weights of products recovered, following distillation of the volatiles, are oligomers with $M_n \approx 2,000$ D.

This approach to the preparation of high molecular weight polysilazanes is not useful because catalytic cleavage of Si-N bonds in cyclomers occurs at approximately the same rate as cleavage of Si-N bonds in the oligomers; thus, chain growth will not occur. However, the fact that equilibration is extremely rapid originally suggested the involvment of Si-H/H-N dehydrocoupling reactions during equilibration. This in turn led to the original concept of preparing polysilazane polymers via catalytic dehydrocoupling [29] as discussed above.

Future Directions

The potential utility of catalysis as a synthetic tool for the preparation of organometallic polymers is just being realized. Much of this potential remains undeveloped. Opportunities for research lie both in optimization of catalyst design and catalyst selectivity for the reactions described above. Additional opportunities most probably remain in the development of new bond forming reactions involving second and third row elements (e.g. dehydrocoupling reactions involving P-H and Ge-H bonds).

Finally, combined reactions where organometallics are copolymerized with organics may also be an extremely fruitful area of research.

Acknowledgments

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Catalytic Synthesis of Polymethylsilsesquioxanes

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Abstract:

Dimethyltitanocene, Cp_2TiMe_2, where $Cp = C_5H_5$, can be use to promote the redistribution of -$[MeHSiO]_x$- cyclomers and linear oligomers to produce a polymethylsilsesquioxane copolymer of the type -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$-. A mechanism for this redistribution is suggested, that involves s-bond metathesis promoted by a Ti(IV) species. The structural evolution of the polymethylsilsesquioxane copolymer as it is heated to 1000 °C is followed using solid state ^{29}Si NMR. TGA experiments and chemical analysis support the NMR results which indicate that most of the starting monomer is either volatilized or undergoes further redistribution, so that by 400 °C only polymethylsilsesquioxane remains.

The active catalyst derived from Cp_2TiMe_2 will also catalyze the alcoholysis of the Si-H bonds in the copolymer producing alkoxy derivates, -$[Me(RO)SiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- (R = Me, Et, nPr, nBu). This same catalyst system can be used to polymerize polysilazane oligomers such as -$[MeHSiNH]_x$- or -$[H_2SiNMe]_x$-, but only if some -$[MeHSiO]_x$- is present. The ceramic yields of 1:1, 1:3, 1:9, and 1:18 ratios of -$[MeHSiO]_x$-:-$[MeHSiNH]_x$- were much higherthan that found for the pure polysilazane. At higher ratios of polysilazane, the apparent ceramic composition was the same as that found for the pure polysilazane.

Introduction. Silsesquioxanes, $RSi(O)_{1.5}$, represent a unique and poorly studied subset of polyalkylsiloxanes. This is despite the fact that they offer many exceptional properties. For example, silsesquioxanes, because of their need to form three Si-O-Si bonds, assume regular polyhedral shapes such as shown for octamethyloctasilsesquioxane:[1]
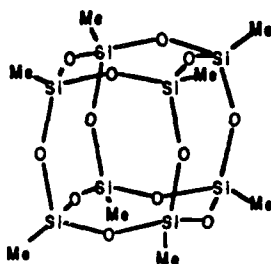
These polyhedral shapes have geometries very similar to those found for silica and its derivatives. Feher et al[2] have used this similarity as the basis for developing molecular models of silica surfaces. The regular geometry also contributes to such properties as high temperature stability[1] and high hardness.[3] Octamethyloctasilsesquioxane is stable in air to 415°C at which temperature it sublimes.

Polysilsesquioxanes appear to have cage rather rather than ladder structures,[4] wherein the polymer is formed by opening of a polyhedral edge as suggested for polymethylsilsesquioxane:
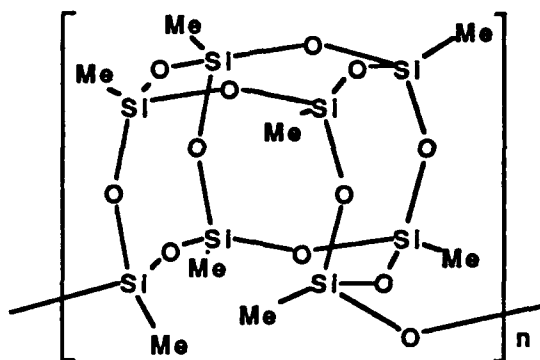

Polymethylsilsesquioxane, $-[MeSi(O)_{1.5}]_x-$, is stable in air to temperatures $>500°C$ and, as we will show below, to at least 600°C in nitrogen. The phenyl derivative is reported to be stable to temperatures of 800°C.[1] The cage structure has been suggested to be useful for making microporous materials.[5]

Polymethylsilsesquioxanes have been used as protective polymer coatings in the electronics industry[6] and as precursors to silica and $SiO_{4-x}C_x$ glasses:[7]

900°C/O₂

1200°C/N₂

70% SiO₂, 20% SiC and 10% C
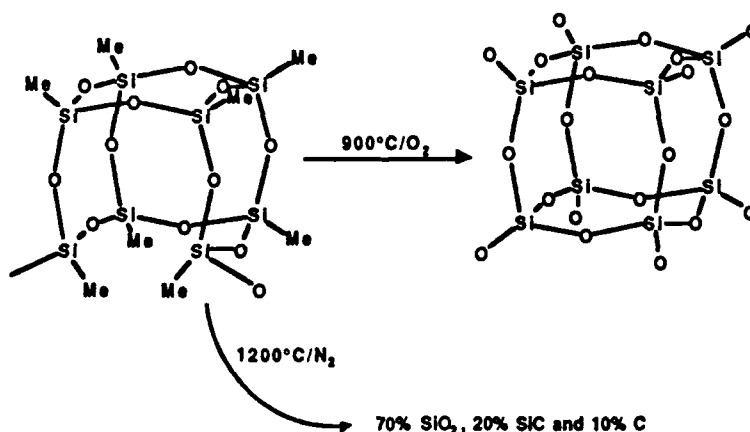
From an engineering standpoint, these materials offer exceptional properties that should lead to widespread applications. Unfortunately, their propensity for forming gels makes it extremely difficult to prepare useful, processable quantities of any given material.

Until recently, the only method of preparing silsesquioxanes was via hydrolysis of the alkyltrichloro or trialkoxysilane:[1,2,5]
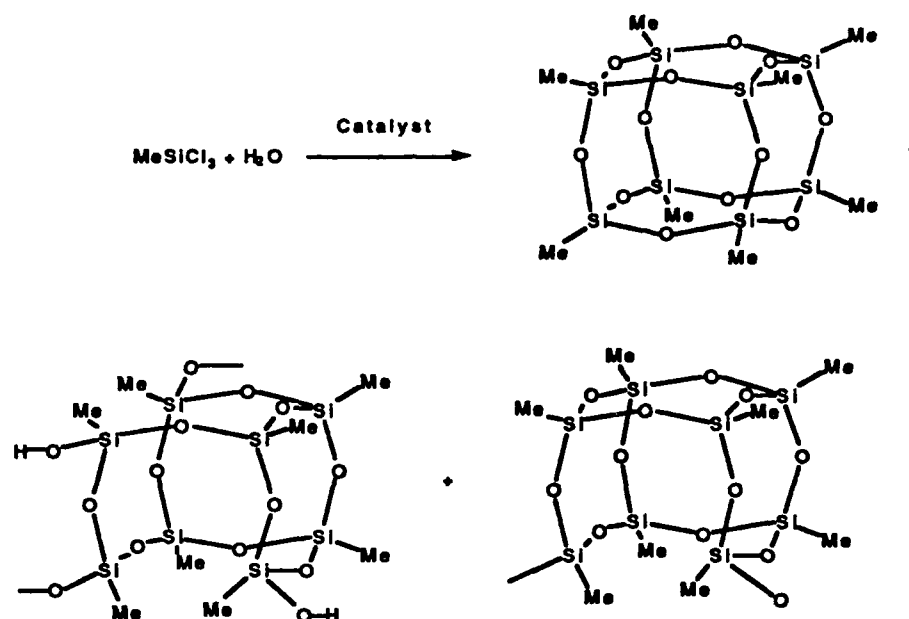
Separation of the polyhedral or polyalkylsilsesquioxane from the reaction mixture is extremely difficult and the isolable yields for these compounds are quite poor, typically ranging from 15-30%. Consequently, the discovery by one of us that titanium will catalyze the redistribution of alkoxysilanes under extremely mild conditions, reaction (1),[8] suggested that

$$3MeHSi(OEt)_2 \xrightarrow{<0.1 \text{ mol } \% \text{ Cp}_2\text{TiMe}_2/\text{RT}} MeSiH_3 + 2MeSi(OEt)_3 \qquad (1)$$

it might be possible to synthesize polysilsesquioxanes via a similar route which eliminates the need for a hydrolytic synthesis:

$$-[MeHSiO]_n- \xrightarrow{<0.1 \text{ mol } \% \text{ Cp}_2\text{TiMe}_2/\text{RT}} MeSiH_3 + -[MeSi(O)_{1.5}]_x- \qquad (2)$$

This reaction works very effectively and we present here an overview of our recent efforts to prepare and characterize the resulting polymers and their properties. The work presented here includes work previously published elsewhere.[9,10]

Results and Discussion:

Neat mixtures of either cyclic $-[MeHSiO]_n-$ (n =4,5), or linear oligomeric, $Me_3Si-[MeHSiO]_n-H$ ($M_n \approx 2000$ D) with 0.2 mol % $(h^5-C_5H_5)_2TiMe_2$ will turn royal blue (under N_2 at 20°C) following an induction period of ca 15 min. $MeSiH_3$ is evolved rapidly with stirring and in 5-7 min the solution becomes extremely viscous and gels in 10-15 min. Solid state ^{29}Si NMR (see below) indicates that the

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final gel consists of a copolymer of approximate composition -[MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$-. The induction period that precedes reaction appears to be related to free radical promoted decomposition of (h^5-C$_5$H$_5$)$_2$TiMe$_2$ which generates the true catalyst.
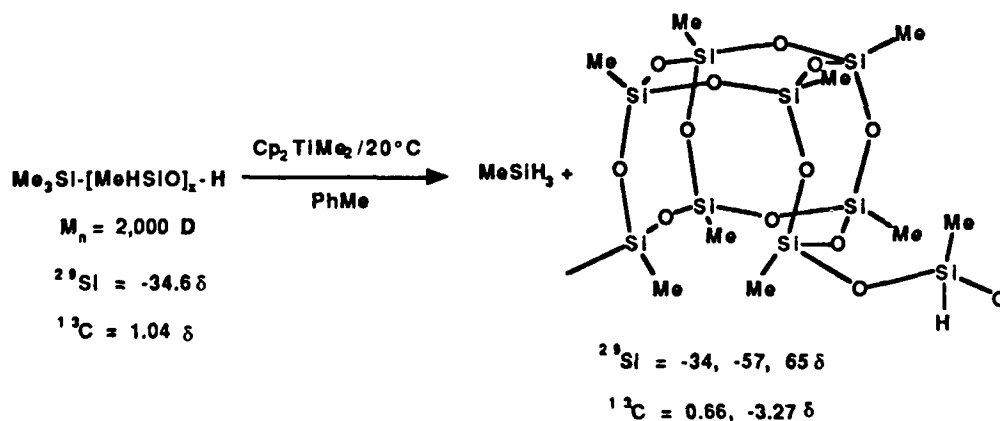
Soluble product can be obtained by dilution with toluene. Thus, reaction in a five-fold excess (with respect to added -[MeHSiO]$_n$-) of toluene gives a stable solution after 72 h of reaction. Reactions attempted with less than a five-fold excess of toluene lead inevitably to the formation of a gel.

Thin films cast from the resulting copolymer/toluene solution exhibit moderate elastomeric properties, excellent adhesion to glass, carbon, and metal surfaces and, can be heated without significant changes in properties to 250°C. Above this temperature, the polymer becomes more and more brittle; however, no visible degradation occurs up to temperatures of approximately 400°C. However, solid state ^{29}Si NMR can be used to demonstrate that structural changes do occur on heating.

Because of our continuing interest in polymer precursors to ceramics we followed the structural evolution of the Me$_3$Si-[MeHSiO]$_n$-H derived copolymer during heating to 1000°C using solid state ^{29}Si NMR (Figure 1). At room temperature, we see the Me$_3$Si (3%) and Me(OH)Si (4%) end caps of the original oligomer together with peaks for -[MeHSiO]$_n$- (30%) and -[MeSi(O)$_{1.5}$]$_x$- (70%). TGA experiments and chemical analysis[9] support the NMR results which indicate that most of the starting monomer is either volatilized or undergoes further redistribution such that by 400°C only the pure polymethylsilsesquioxane remains. Note that in the NMR the sharp singlet of the [MeSi(O)$_{1.5}$] silicon is present at 600°C but becomes very broad as the polymer is transformed into a glass at 800°C.[10]

Insert Figure 1

Nearly identical copolymer compositions are obtained from the copolymer generated in toluene as determined following solvent removal. The NMR established composition is confirmed by the chemical analysis.[11] Given the relatively simple ^{29}Si NMR, the copolymer structure is assumed to be that shown below:

Me$_3$Si-[MeHSiO]$_x$-H $\xrightarrow[\text{PhMe}]{\text{Cp}_2\text{TiMe}_2/20°\text{C}}$ MeSiH$_3$ +

M_n = 2,000 D

^{29}Si = -34.6 δ

^{13}C = 1.04 δ

^{29}Si = -34, -57, 65 δ

^{13}C = 0.66, -3.27 δ

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However, it is possible that other polyhedral silsesquioxane structural units also form in the copolymer.

Catalytic redistribution of hydridosiloxanes by transition metals was first reported by Curtis and Epstein.[12] They discovered that iridium complexes promoted redistribution of H-$[Me_2SiO]_x$-$SiMe_2H$ and proposed the following type of mechanism:
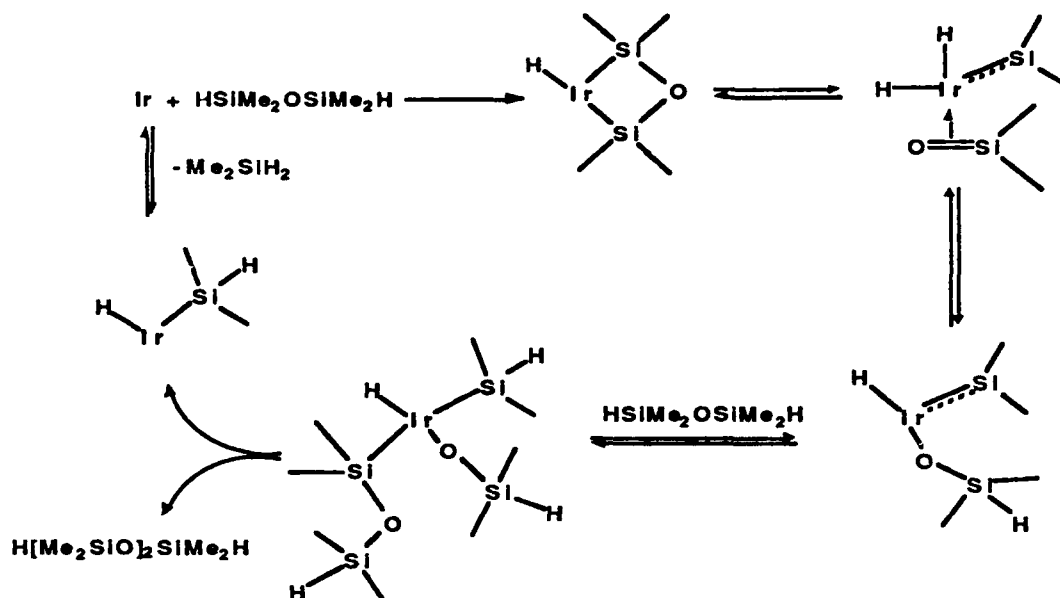

Based on recent work by Tilley et al[13] on the reactions of d^0 metals with silanes, we believe that a different mechanism is operating here. This mechanism probably involves s-bond metathesis promoted by a Ti (IV) species generated by decomposition of $(h^5$-$C_5H_5)_2TiMe_2$. The following mechanism is suggested based on the work of Tilley et al; however, substantiation must await detailed kinetic studies.
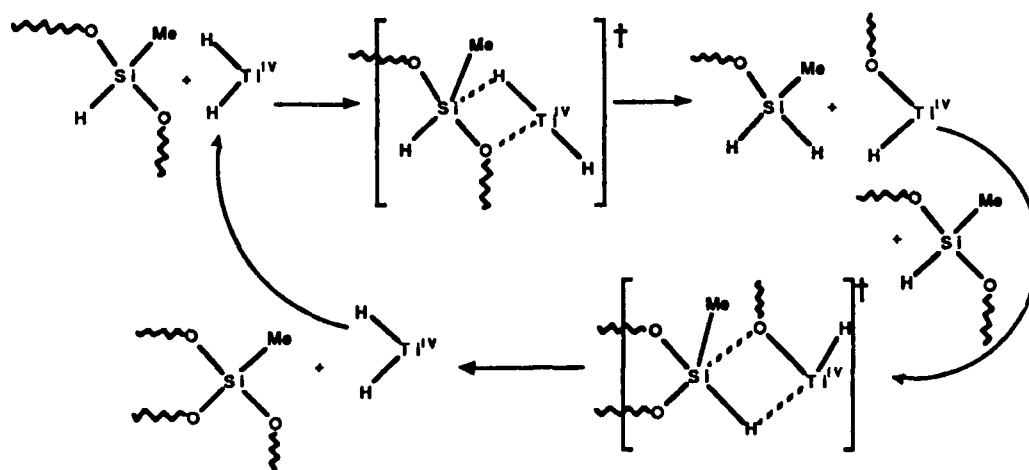
We propose a Ti (IV) catalytic process despite the royal blue color of the reaction which is typical Ti (III) compounds and despite our having isolated Ti (III) complexes[14] in related systems because of the following discovery.

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Because the copolymer -[MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$- still retains Si-H groups which are susceptible to further modification either by hydrosilylation or alcoholysis, we explored the possibility of changing the copolymer rheological characteristics by reaction with alcohols. We find that addition of alcohols to the toluene reaction solution anytime during the course of reaction leads to very effective alcoholysis of the copolymer:

$$+ \; ROH \xrightarrow[\text{PhMe}]{\text{Cp}_2\text{TiMe}_2/20°\text{C}} H_2 +$$

R = Me, Et, nPr, nBu
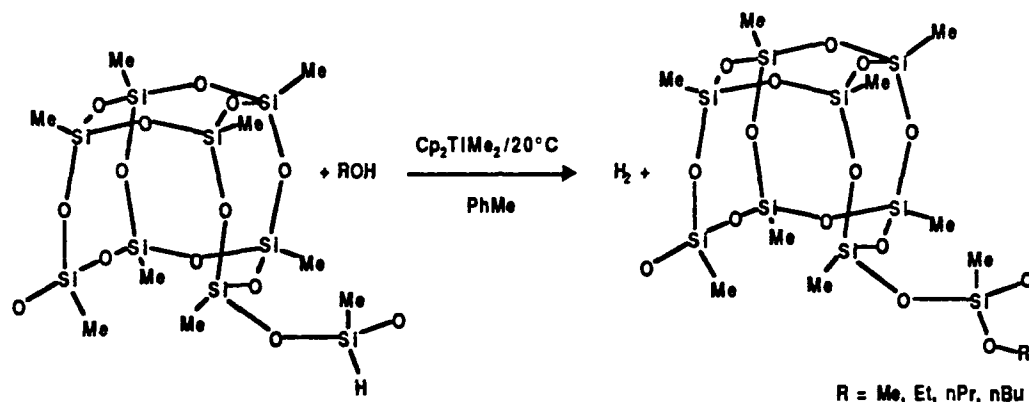
The addition of MeOH leads to a rapid color change from royal blue to yellow orange and extremely rapid (almost violent) evolution of hydrogen. The reaction is complete within the time of addition. The other alcohols are less reactive, with the n-BuOH reaction taking 1-2 days at room temperature.

Once solvent is removed, the methoxy derivative will become gel-like in hours to days depending on the temperature of the room. The n-butoxy derivative in contrast is much less susceptible to gelling and will remain as a viscous liquid for periods up to one week. N-propanol solutions of the n-propoxy derivative (25 wt %) will remain stable almost indefinitely. NMR characterization indicates the formation of -[Me(RO)SiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$- and confirms the initial copolymer composition.[10] These polymers are actually a masked form of -[MeSi(O)$_{1.5}$]$_x$- given that addition of water will lead to hydrolysis of the SiOR bond and water can actually be used to cause thermosetting!

The yellow-orange color is typical of a Ti (IV) catalyst and when coupled with Tilley's work suggests the above proposed Ti (IV) promoted redistribution reaction.

Polysilazane Polymerizations[15]

The success of this catalyst system suggested that it might also be used for the catalytic polymerization of polysilazane oligomers such as -[MeHSiNH]$_x$- or -[H$_2$SiNMe]$_x$-. This would offer an alternative to the ruthenium catalysts that we have previously used to form tractable silicon nitride preceramic polymers. To our suprise, neither oligomer underwent catalytic redistribution when mixed with (h^5-C$_5$H$_5$)$_2$TiMe$_2$ despite the fact that the catalyst reacted and some small amount of gas (presumably CH$_4$) evolved coincident with reaction.

This result was disappointing; however, we attempted to catalyze redistribution of -[MeHSiO]$_x$- in the presence of -[MeHSiNH]$_x$- to explore the possibility of trapping the -[MeHSiNH]$_x$- oligomer in the resulting silsesquioxane gel. We used ceramic yield as a measure of our success. Thus, Figure 2 shows TGAs for the copolymer derived from -[MeHSiO]$_x$- (74-78% ceramic yield at 900°C /N$_2$), pure

-[MeHSiNH]$_x$- (37% ceramic yield at 900°C/N$_2$) and a 1:1 mixture of -[MeHSiO]$_x$-/-[MeHSiNH]$_x$-. If the 1:1 mixture were to act simply as a physical mixture, then the ceramic yields for the combination should be the arithmetic mean or 56%. Instead, we find that (see Figure 2) the ceramic yield is ≈ 72%. This would suggest that we were successful in trapping the silazane in the interstices of the polymethylsilsesquioxane gel. However, an alternate explanation is that in the presence of the hydridosiloxane, the catalyst is now capable of catalyzing redistribution of polysilazanes. To test this, we changed the siloxane:silazane ratio. Table 1 shows both that as the ratio is changed from 1:1 to 1:3 to 1:18 reaction continues to occur, the ceramic yields stay high (relative to pure polysilazane) and the resulting ceramic products begin to look like the ceramic products obtained from pure -[MeHSiNH]$_x$-. Our preliminary conclusion is that titanium catalyzed redistribution of -[MeHSiNH]$_x$-requires the presence of some quantity of hydridosiloxane as cocatalyst.[15]

It is important to note here that the apparent compositions reported in Table 1 are a form of book-keeping that is not truly indicative of the actual nature of the SO$_{4-x}$C$_x$ glass.[9] However, these compositions are adequate for describing the selectivity to ceramic products, at 900°C, obtained by pyrolysis of -[MeHSiNH]$_x$- and -[H$_2$SiNMe]$_x$-. The siloxane/silazane mixtures are perhaps better treated as mixtures of silicon oxynitride, Si$_2$ON$_2$ and SO$_{4-x}$C$_x$ or Si$_2$ON$_2$ and silicon nitride/carbide depending on the percentage of initial hydridosiloxane.

Compound	Ceramic Yield	Apparent Ceramic Composition		
		Si$_3$N$_4$	SiC	C(x's)
MeHSiNH	65	64	25	10
H$_2$SiNMe	63	75	--	18
MeHSiO	78	70 SiO$_2$	20	10
1:1 MeHSiO/MeHSiNH	72	31	20	10
1:9 MeHSiO/MeHSiNH	64	53	22	10
1:19 MeHSiO/MeHSiNH	63	62	19	11

Table 1. Apparent Ceramic Compositions for Selected Polysilazanes, Polymethylsilsesquioxane and Various Mixtures Pyrolyzed to 900°C in Nitrogen. Heating rate 5°C/min. Apparent ceramic compositions calculated assuming Si is the limiting element. N is the limiting element when -[H$_2$SiNMe]$_x$- is the preceramic.

Conclusions

Titanium catalyzed redistribution of -[MeHSiO]$_x$- provides a useful route to tractable, processable methylhydridosiloxane-methylsilsesquioxane copolymers. The "Ti" catalyst active in the redistribution reaction will also promote alcoholysis of the resultant copolymers to produce alkoxy derivatives which display equivalent or slightly better, high temperature stability than the starting copolymer and more controllable rheology.

Although Cp$_2$TiMe$_2$ will not catalyze the polymerization of pure -[MeHSiNH]$_x$-, in the presence of small amounts of hydridosiloxane, it is an active catalyst precursor and permits catalytic redistribution that leads to a high ceramic yield silicon nitride precursor.

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Figure 1. Chemical evolution of Me_3Si-$[MeHSiO]_n$-H derived copolymer during heating to selected temperatures1000 °C using solid state ^{29}Si NMR. M = Me_3SiO; D = $Me_2Si(O)_2$; DH = $MeHSi(O)_2$; DOH = $MeSi(OH)(O)_2$; T = $MeSi(O)_3$; and Q = $Si(O)_4$.

Figure 2. Thermogravimetric Analysis of -$[MeSi(O)_{1.5}]_x$- (a), -$[MeHSiNH]_x$- (c), and a 1:1 Copolymer of -$[MeHSiNH]_x$- and -$[MeSi(O)_{1.5}]_x$- (b). Pyrolyzed under N_2 at a heating rate of 5 °C /min.

THE CATALYTIC SYNTHESIS OF INORGANIC POLYMERS FOR HIGH TEMPERATURE APPLICATIONS AND AS CERAMIC PRECURSORS

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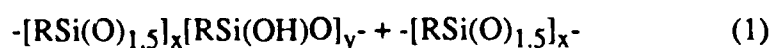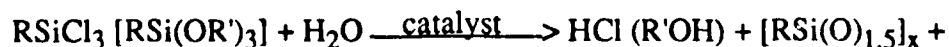
ABSRACT:

Polysilsesquioxanes,-$[RSi(O)_{1.5}]_x$-, exhibit many properties that are potentially quite useful for industrial applications. These properties include high temperature stability ($\approx 600°C$ in O_2); good adhesion and, liquid crystal-like behavior for some derivatives. Moreover, $[MeSi(O)_{1.5}]_x$, polymethyl- silsesquioxane has been used successfully as a precursor for the fabrication of carbon fiber/"black glass" ($SiO_2/SiC/C$) composites and "black glass" fibers. Current methods of preparation depend on hydrolysis of $RSiCl_3$ or $RSi(OR)_3$. Unfortunately, this approach leads to several products that are difficult to purify because polysilsesquioxanes exhibit a great propensity for forming gels. We describe here a simple catalytic approach to the synthesis of polymethylsilsesquioxane copolymers, e.g. $[MeRSiO]_3[MeSiO_{1.5}]_7$ where R = H, OMe, OEt, OnPr and OnBu. The R = H copolymer is produced by catalytic redistribution of -$[MeHSiO]_x$- oligomers using dimethyltitanocene, Cp_2TiMe_2 as the catalyst precursor. Following catalytic redistribution, the resulting copolymer, -$[MeHSiO]_3[MeSi(O)_{1.5}]_7$-, reacts *in situ* with R'OH, R' = Me, Et, nPr and nBu, to produce -$[Me(R'O)SiO]_3[MeSi(O)_{1.5}]_7$-, masked forms of $[MeSi(O)_{1.5}]$. These new copolymers were characterized by ^{1}H, ^{13}C and ^{29}Si NMR, TGA and DTA.

INTRODUCTION

Polysilsesquioxane polymers,[1] -$[RSi(O)_{1.5}]_x$-, represent a very poorly exploited area of polysiloxane chemistry despite the fact that they exhibit a variety of potentially useful properties including: high temperature stability in air;[2] good adhesion to a wide variety of substrates[3] and, in some instances, liquid crystal-like behavior.[1] Moreover, -$[MeSi(O)_{1.5}]_x$-, polymethylsilsesquioxane has been used as a preceramic polymer for fabrication of silicon carbide powders,[4] "black glass" (70% SiO_2/20% SiC/10% C) composite matrices for carbon fibers[5] and for the fabrication of black glass fibers.[6]

The primary problems associated with using polysilsesquioxanes for engineering applications are: (1) the lack of good, high yield synthetic routes and, (2) the highly crosslinked nature of the polymers which limits their tractability and ease of purification. Literature syntheses generally rely on the hydrolysis of $RSiCl_3$ or $RSi(OR')_3$:[1]

$$RSiCl_3 [RSi(OR')_3] + H_2O \xrightarrow{\text{catalyst}} HCl (R'OH) + [RSi(O)_{1.5}]_x +$$
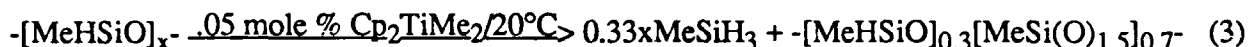
$$-[RSi(O)_{1.5}]_x[RSi(OH)O]_y- + -[RSi(O)_{1.5}]_x- \qquad (1)$$

These reactions usually lead to the coincident formation of polyhedral oligosilsesquioxanes, $[RSi(O)_{1.5}]_x$, where x = 8, 10, 12; polysilsesquioxanes with partially condensed monomer units, $-[RSi(O)_{1.5}]_x[RSi(OH)O]_y-$, and polyhedral polysilsesquioxane itself. Because polysilsesquioxanes exhibit a strong propensity to form intractable gels with organic solvents, there are significant problems with purification which result in low yields. Thus, this synthetic route is unattractive for the rapid, large-scale preparations.

Harrod and coworkers have recently developed a novel titanium catalyzed redistribution reaction, as illustrated in reaction (2),[7] that can also be used to prepare methylsilsesquioxane copolymers,

$$3MeHSi(OEt)_2 \xrightarrow{0.05 \text{ mole } \% \text{ } Cp_2TiMe_2/20°C} MeSiH_3 + 2MeSi(OEt)_3 \qquad (2)$$

reaction (3):[2,8]

$$-[MeHSiO]_x- \xrightarrow{.05 \text{ mole } \% \text{ } Cp_2TiMe_2/20°C} 0.33xMeSiH_3 + -[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}- \qquad (3)$$

The copolymer $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ forms as a gel if neat oligomethylhydridosiloxane, $Me_3SiO-[MeHSiO]_x-H$ ($M_n \approx 2K$ D), is exposed to the catalyst. Fortunately, gelation can be avoided if polymerization is conducted in toluene with a greater than 5:1 toluene to $-[MeHSiO]_x-$ volume ratio. The resulting polymer can be used to prepare coatings, fibers and monolithic shapes.[8] At lower volume ratios, gels form quite readily.

Although the 5:1 volume ratio solutions can be used for some applications, the gel-like material that results on solvent removal limits the copolymer's utility for some applications, e.g. as a matrix material for composites. As such, we sought to modify the copolymer's physical characteristics by taking advantage of the reactive Si-H bonds. Reactions at these bonds should permit one to vary the side chains on the copolymer backbone and thereby control some of its physical properties.

The long term objectives of the work described here are to prepare tractable silsesquioxane copolymers that exhibit improved high temperature performance and that are also useful for the fabrication of polymer and ceramic, membranes and fibers. This report concerns preliminary studies on the modification of the $-[MeHSiO]_x[MeSi(O)_{1.5}]_y-$ copolymer by alcoholysis of Si-H bonds.

RESULTS AND DISCUSSION

The copolymer produced in reaction (3) either neat or in toluene gives the same results when characterized by magic angle spinning (MAS), multinuclear NMR, solution NMR, diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), chemical analysis, TGA or DTA. These extensive studies are described elsewhere.[2,7] For illustration purposes, the TGA of $-[MeHSiO]_{0.3}$- $[MeSi(O)_{1.5}]_{0.7}-$ is shown below (Figure 1). This Figure also contains the elemental analyses (at selected temperatures) as the polymer is heated in nitrogen at 5°C/min to 900°C.

At 400°C, the elemental analysis corresponds to pure $-[MeSi(O)_{1.5}]_x-$ without any of the starting

monomer. This is confirmed by the MAS ^{29}Si NMR which shows a single peak at -65.7 d relative to TMS.[2] Consequently, the 20% weight loss at temperatures below 400°C corresponds to the depolymerization and volatilization of almost all of the -[MeHSiO]$_x$- units.

Copolymer Preparation and Characterization

Efforts to modify the -[MeHSiO]$_x$[MeSi(O)$_{1.5}$]$_y$- copolymer began with attempts to promote alcoholysis of the Si-H groups, reaction (4),[9,10] *in situ*, following completion (72 h) of reaction (3).

-[MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$- + ROH $\underline{\text{0.5 mole % Cp}_2\text{TiMe}_2\text{/20°C}}$ >

$$H_2 + \text{-[Me(RO)SiO]}_{0.3}\text{[MeSi(O)}_{1.5}\text{]}_{0.7}\text{-} \qquad (4)$$

The motivation for the alcoholysis experiments was to create a polysilsesquioxane wherein some of the T groups, [MeSi(O)$_{1.5}$], are masked as the alkoxy derivative, [MeSi(O)OR]. In this way, the yield of T groups in the polymer would increase significantly. Moreover, if R is a long chain alkyl group it would also be possible to introduce more flexibility and perhaps reduce or eliminate the elastomeric or gel character.

To our surprise, the addition of alcohols rapidly extinguishs the royal blue Ti(III) color of the original active catalyst system that forms in reaction (3) leaving a yellow solution. If the alcohol is MeOH, then rapid, almost violent H$_2$ evolution ensues coincident with the color change. The reaction can be somewhat exothermic depending on the initial catalyst concentration.

Removal of the solvent and characterization by NMR indicates that almost all of the Si-H bonds react with alcohol converting the remaining silicons to T groups. NMR characterization, Table 1, confirms the 30:70 composition of the initial copolymer in that the integrated ratios of the alkoxy groups to T groups in the product copolymer are nearly the same.

To date, we have made the derivatives R = Me, Et, Pr, nBu and bis-1,4-(2-hydroxyethoxy)benzene (hydroquinone). These alcohols exhibit reactivities with the copolymer strictly in accord with the size of the alkyl group. The MeOH reaction is quite vigorous and is over in minutes to hours while the nBuOH reaction requires two to three days. The hydroquinone reaction results in extensive crosslinking that makes further characterization impossible. The other copolymers are moderately (MeO-) to completely (nBuO-) tractable following solvent removal; however, it is expedient to redissolve the polymer in the corresponding alcohol as these polymers still show a tendency to gel with time (days to weeks).

The alkoxy copolymers have been characterized by ^{1}H, ^{13}C and in part by ^{29}Si as recorded in Table 1. The ^{13}C shifts of the alkoxy carbon bound directly to the oxygen are quite similar (except for MeO). Consequently, characterization by ^{29}Si was not deemed essential in all instances. The proton and carbon spectra are all standard values for alcohols or alkoxy substituents. However, the ^{29}Si results are interesting because they provide some understanding of the polymer backbone

OR'	^{29}Si(d)	^{13}C(d)	^{1}H(d) (integration)
Starting oligomer	-34.6	1.75 OSi(CH$_3$)$_3$ 1.04 SiCH$_3$	4.69 (3.43) MeHSiO 0.18 (1.02) OSi(CH$_3$)$_3$ 0.10 (9.68) HSiCH$_3$
H (72 h)	-33.5, -34.4, -35.9 -57.2, -65.5	1.68 OSi(CH$_3$)$_3$ 0.66 HSiCH$_3$ -3.27 OSiCH$_3$	4.68 (8) SiH 0.18 (x) OSi(CH$_3$)$_3$ 0.13 (80-x,y) HSiCH$_3$ 0.10 (y) OSiCH$_3$
OCH$_3$		49.70 OCH$_3$ 1.54 OSi(CH$_3$)$_3$ -3.29 br OSiCH$_3$ -5.10 br MeOSiCH$_3$	4.70 (1.7) SiH 3.48 (17) OCH$_3$ 0.13 (49-x) OSiCH$_3$ 0.10 (x) MeOSiCH$_3$
OCH$_2$CH$_3$		57.99 OCH$_2$ 18.16 CH$_2$CH$_3$ 0.70 br ROSiCH$_3$ -3.25 br OSiCH$_3$	3.76 (7) OCH$_2$ 1.20 (10) CH$_2$CH$_3$ 0.12 SiCH$_3$
O(CH$_2$)$_2$CH$_3$	-36.7, -57.9, -66.3	64.02 OCH$_2$ 25.55 OCH$_2$CH$_2$ 10.27 CH$_2$CH$_3$ 1.65 OSi(CH$_3$)$_3$ -3.12 OSiCH$_3$ -4.52 ROSiCH$_3$	4.70 (3) HSiCH$_3$ 3.65 (6.4) OCH$_2$ 1.55 (8) OCH$_2$CH$_2$ 0.87 (8) CH$_2$CH$_3$ 0.12 (33-x) OSiCH$_3$ 0.10 (x) OSiCH$_3$
O(CH$_2$)$_3$CH$_3$	-36.5 w, -57.94, -64.33, -66.45	62.10 OCH$_2$ 34.50 OCH$_2$CH$_2$- 18.94 CH$_2$CH$_3$ 13.82 CH$_2$CH$_3$ -3.0 ->-3.5 OSiCH$_3$	3.68 (8.6) OCH$_2$ 1.50 (9) OCH$_2$CH$_2$ 1.34 (8) CH$_2$CH$_3$ 0.89 (11) CH$_2$CH$_3$ 0.12 (30) SiCH$_3$

Table 1. NMR Spectra for -[-Me(OR)SiO]$_x$[MeSi(O)$_{1.5}$]$_y$-. Spectra taken in CDCl$_3$ using TMS as an internal standard.

structure if we use published ^{29}Si peak assignments for standard siloxane monomer units.[11]

The ^{29}Si and ^{13}C spectra for Me$_3$SiO[MeHSiO]$_x$H, (M$_n$ ≈ 2K D), the starting oligomer, are simple. The MeHSiO ^{29}Si peak appears at -34.6 d. The product, [MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$,

obtained from Ti catalyzed redistribution, shows several ^{29}Si peaks in the same vicinity, -33 to -36 d. It also shows two peaks at -57.2 and -65.5 d. These results, when coupled with the reproducible 30:70, [MeHSiO] : [MeSi(O)$_{1.5}$] ratio, suggest a polymer structure consisting of open cubes of T groups bridged by one or two -MeHSiO- groups as depicted below. By visual inspection, the peak at -57.2 d is much smaller than the peak at -65.5 d.

Consequently, we assign this peak to the open silicons in the cube and the -65.5 d peak to the remaining T group silicons in the cube. In the nBuO- derivative, the -34.6 d peak is replaced by the appearance of a peak at ca. -64 d . This peak appears to overlap with the T groups in the cube in the nPrO derivative. We assign this peak to the alkoxy substituted silicons.

High Temperature Studies

TGA studies indicate that the high temperature stability of the alkoxy derivatives is very similar to that of the starting copolymer. The 900°C ceramic yields for the set of copolymers are 76% (MeHSiO), 75% [Me(MeO)SiO], 74% [Me(EtO)SiO], 78% [Me(nPrO)SiO] and 62% for the [Me(nBuO)SiO] derivative. As in Figure 1, most of the weight loss occurs below 400-450°C. If weight loss in the alkoxy derivatives occurs by a mechanism similar to that found for the hydrido copolymer, then weight loss must occur by depolymerization and volatilization of Me(RO)SiO groups. One would expect increasing weight losses with increases in the size of the R' group. Clearly this is not the case with the R' = Me, Et or nPr derivatives. In these cases, the ceramic yields are comparable to that of the original copolymer. Even in the nBuO- derivative, the mass of the group increases from 60 D (MeHSiO) to 132 D [Me(OnBu)SiO]. If complete loss of 60 D leads to a ceramic yield of 75% then complete loss of 132 D should lead to a ceramic yield of <50%. These results inidcate that the ceramic products from pyrolysis of these materials retain the carbons in the alkoxy groups.

This is in contrast to studies by Fox et al.[4] on the pyrolysis of the polyalkylsilsesquioxanes, -[RSi(O)$_{1.5}$]$_x$-, where increasing the size of R from Me to Et to Pr resulted in drops in the 900°C ceramic yields from 86% (Me) to 47% (Et) to 44% (nPr). In all instances, except for the Me derivative, our ceramic yields are much higher.

It is likely that these differences arise because the bond dissociation energy for Si-C bonds is approximately 85-90 kcal/mole whereas O-C bond dissociation energies are typically around 100 kcal/mole.[12] Thus, the decomposition mechanisms for the two types of polymers are quite different. The important point to be made is that proportionately, the EtO- and nPrO- derivatives incorporate more carbon in the ceramic product than the EtSi and nPrSi derivatives, which should result in a higher proportion of SiC in the final composite ceramic/black glass.

ACKNOWLEDGEMENTS

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Synthesis and High Temperature Chemistry of Methylsilsesquioxane Polymers Produced by Titanium Catalyzed Redistribution of Methylhydridooligo- and polysiloxanes.

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Abstract: Homogeneous, titanium catalyzed redistribution of the cyclomers -[MeHSiO]$_x$- (x = 4 or 5) or the linear oligomer -[MeHSiO]$_x$- (M$_n$ ≈ 2,000 D) generates MeSiH$_3$ and a copolymer of approximate composition -[MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$-. The high temperature behavior of this copolymer follows closely that of similar polymers prepared by sol-gel processing. Heating to 900°C at 5°C/min/N$_2$ gives a black glass (75% ceramic yield) with an apparent composition of SiO$_2$ (70%); SiC (20%) and C (10%). This composition belies the true nature of this amorphous material which is best described by the various Si-E bonding arrangements (E = O, C, H).

The chemical evolution of the copolymer during heating is followed by MAS NMR, TGA, DRIFT spectroscopy and chemical analysis at selected temperatures up to 1000°C. Heating to 400°C results in a loss of 20 weight percent of the starting copolymer. Chemical analysis and NMR indicate that this weight loss is associated with the disappearence of most of the -[MeHSiO]$_x$- portion of the copolymer and that the 400°C material consists primarily of -[MeSi(O)$_{1.5}$]$_x$-. Sharp absorption bands in the FTIR and resonances in the various NMR spectra associated with recognizable structural features (e.g. Si-CH$_3$) in the low temperature polymeric material, give way to broad, poorly defined absorptions and resonances at temperatures above 600°C. The changes are indicative of the transformation from a polymer to a glass.

Above 600°C, the silsesquioxane CH$_3$ groups react with Si-O bonds to generate Si-OH bonds, Si-H bonds and new Si-C bonds. These reactions illustrate the basic chemistry involved in the carbothermal reduction of SiO$_2$ and the polymer degradation pathways. The resulting glassy material consists of species containing 4, 3 or 2 Si-O bonds with the remaining bonds being either Si-C or Si-H.

Heating the copolymers in O$_2$ gives ceramic yields of > 90% of SiO$_2$. Based on this result, silsesquioxanes offer an alternative to sol-gel processing of silica glasses.

Introduction

Silsesquioxanes, $[RSi(O)_{1.5}]_n$, have recently been explored as models for silica surfaces[1] and particles;[2] as precursors to nitrided glasses[3] (in the presence of NH_3) and silicon oxynitride (Si_2ON_2);[4] as precursors to silicon carbide powders[5] and silicon carbide reinforced (black) glass composite matrices;[6] as cladding materials for optical fibers[7] and, as photoresists.[8] The typical synthesis involves the hydrolysis of the corresponding silyl chloride, $RSiCl_3$, in the presence of a catalyst (acid or base) in an appropriate organic solvent:[9]

$$RSiCl_3 + 2\text{-}3H_2O \xrightarrow{\text{catalyst}} 3HCl + \text{-}[RSi(O)_{1.5}]_x\text{-} \qquad (1)$$
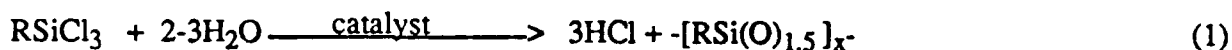
Although represented by $\text{-}[RSi(O)_{1.5}]_x\text{-}$, the products of reaction (1) are normally a mixture of polyhedral polysilsesquioxanes, polyhedral oligosilsesquioxanes, $[RSi(O)_{1.5}]_x$ (generally < 40% yield) where x = 6, 8, 10 etc., partially condensed polyhedral silsesquioxanes $\{[RSi(O)_{1.5}]_x[RSi(O)(OH)]_z\}$,[1] and polymeric species that contain silsesquioxane units and uncondensed silanols, e.g. $\text{-}[RSi(O)_{1.5}]_x[RSi(O)_{0.5}(OH)_2]_y[RSi(O)(OH)]_z\text{-}$.[9]
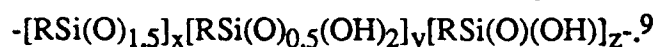
The synthesis of polysilsesquioxanes is of interest to us for a number of reasons. First, alkyl- and arylsilsesquioxanes are uncommonly stable in air at quite high temperatures with $[MeSi(O)_{1.5}]_8$ stable to $\approx 400°C$, $[PhSi(O)_{1.5}]_8$ stable to 500°C and polyphenylsilsesquioxane stable to temperatures of 600°C.[9] Thus, they represent a potential alternative to organic polymers for a wide variety of high temperature applications, providing useful synthetic routes can be developed that permit the preparation of tractable polysilsesquioxanes.

Second, the synthesis of poly-3-tolylsilsesquioxanes results in the formation of mesomorphic lamellar microstructures which indicates that silsesquioxanes may serve as a new class of organometallic liquid crystalline materials.[9] Again, this assumes that useful synthetic routes to tractable materials can be developed.

Third, methylsilsesquioxane, $\text{-}[MeSi(O)_{1.5}]\text{-}$, is the oxygen analog of methylsilsesquiazane, $\text{-}[MeSi(NH)_{1.5}]_x\text{-}$, a type of monomer unit that forms in the synthesis of polysilazane preceramic polymers. Thus, studies of the high temperature chemistry of $\text{-}[MeSi(O)_{1.5}]_x\text{-}$ should provide useful comparisons with the analogous chemistry of $[MeSi(NH)_{1.5}]_x$ preceramics.[10]

Fourth, heating polymethylsilsesquioxane in air or O_2, at temperatures greater than 600°C, leads to the formation of silica in 90+% ceramic yields. This suggests that methylsilsesquioxane polymers may offer an alternative to sol-gel processing of glass materials.[11]

Consequently, the recent discovery by one of us that Cp_2TiMe_2 can be used to catalyze the redistribution of $MeHSi(OEt)_2$, reaction (2),[12] prompted us to explore the utility of synthesizing

$$3MeHSi(OEt)_2 \xrightarrow{Cp_2TiMe_2/20°C} MeSiH_3 + 2MeSi(OEt)_3 \qquad (2)$$

2
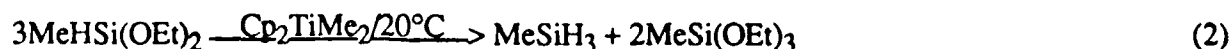
methylsilsesquioxanes, $-[MeSi(O)_{1.5}]_x-$, by catalytic redistribution of methylhydridopolysiloxanes, $-[MeHSiO]_x-$, as illustrated in reaction (3):

$$-[MeHSiO]_x- \xrightarrow{Cp_2TiMe_2} 0.33xMeSiH_3 + -[MeSi(O)_{1.5}]_{0.67x}- \qquad (3)$$
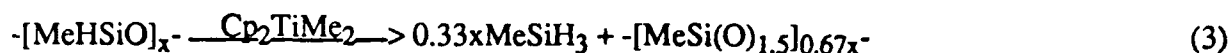
Reaction (3) proceeds quite readily at low temperatures and leads to a unique copolymer of $-[MeSi(O)_{1.5}]_x-$ and $-[MeHSiO]_y-$. We describe here studies that focus on the high temperature chemistry of this copolymer. Our efforts have been guided by the above cited interests and by the fact that we have recently extended reaction (3) to the polymerization of the oligosilazanes $-[MeHSiNH]_x-$ and $-[H_2SiNMe]_x-$.[11,13]

Experimental

General.

The polysiloxanes, $-[MeHSiO]_4-$, $-[MeHSiO]_5-$, and $Me_3Si-[MeHSiO]_x-H$ ($M_n \approx 2,000$) were purchased from Petrarch/Hüls Corp. The cyclomers were distilled under N_2 and stored under N_2 prior to use. The polymer was stored over CaH_2, under N_2 prior to use. Cp_2TiCl_2, $CpTiCl_3$ and $Ti(NMe_2)_4$ (Strem Chemicals) were used as received. $NaBH_4$ and MeLi (Alfa Chemicals) were used as received. Cp_2TiMe_2, $CpTiMe_3$ and Cp_2TiBH_4 were prepared according to literature procedures.[14-16] Elemental analyses were performed by Galbraith Laboratories, Knoxville Tenn.

Instrumental Characterization Methods.

NMR Studies. All solution spectra were run in $CDCl_3$ unless otherwise noted and recorded on a Varian 300 MHz instrument. Proton NMR spectra were obtained with the spectrometer operating at 300 MHz and using a 4000 Hz spectral width, a relaxation delay of 1 s, a pulse width of 82 degrees, and 16K data points. $^{13}C\{^1H\}$ NMR spectra were obtained with the spectrometer operating at 75 Hz and using a 16,000 Hz spectral width, a relaxation delay of 0.5 s, a pulse width of 60 degrees, and 16K data points. $^{29}Si\{^1H\}$ NMR spectra were obtained with the spectrometer operating at 59.6 MHz and using a 32,000 Hz spectral width, a relaxation delay of 15 s, a pulse width of 58 degrees, and 32K data points.

Solid state spectra were recorded on an MSL 400 Brüker spectrometer operating at 79.5, 100.6 and 400 MHz for ^{13}C, ^{29}Si and ^1H respectively. The spinning rate was 4 kHz. For the ^{29}Si and ^1H MAS experiments, pulsewidths of 2.5 μs and 6 μs respectively were used with delays between pulses of 60 s and 4 s. For the CP MAS experiments, contact times of 2 ms were used for ^{29}Si and 1 ms for ^{13}C. Sample sizes for all solid state spectra were $\approx$ 500 mg.

Weight loss experiments were conducted using a Perkin Elmer TGA-7 and or a Perkin Elmer DTA 1700. 20-40 mg samples, prepared as in the pyrolysis experiments (see below), were placed in a platinum pyrolysis boat in N_2 or synthetic air (80% N_2 and 20% O_2) and heated at 5°C/min to temperatures of 900°C.

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) studies were performed using

an IBM FTIR-44 spectrophotometer. Samples were prepared in the dry-box by mixing pyrolysis products with oven dried KBr (stored in the box) in a "Wiggle Bug" cup. The sealed cup was then transferred out of the dry-box to a "Wiggle Bug" (dental ball mill) and pulverized. Once pulverized, the cup was opened and samples were quickly transferred from the cup to the sample holder in air. The sample chamber was flushed with N_2 for a minimum of 15 min before data collection. IR peak positions were identified using a standard peak searching program.

Mass Spectral Fragmentation Studies.

Mass spectral fragmentation data were obtained for the DH_4, DH_5 and the oligo(methylhydrigo)siloxane using a Hewlett Packard 5890 gas chromatograph (GC) coupled to 5970 mass selective detector (MS). The heating schedule for the GC was 40°C $\xrightarrow{10°C/min}$ 280°C. Injector and detector temperatures were 280°C. Sample analysis was initiated following a 2-3 min solvent delay. Scan width from 750-50 m/z. The multiplier was 1000. Data are obtained as m/z = M-1 peaks.

Low temperature mass spectral analysis of the volatile fragments that issue on heating -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- from 150°C to 250°C were obtained by direct probe inlet techniques using a VG 7070H double focussing mass spectrometer with 70 eV electron ionization energy. Data are obtained as m/z = M or M+1.

Standard Catalytic Run and Catalyst Survey. An oven dried, 40 ml pop-bottle glass reactor, containing a stir bar and 5 mg of catalyst was sealed under N_2. Alternately, 5 mg of catalyst was dissolved in 100 μl of hexane and added by syringe. $Ti(NMe_2)_4$ was also added by syringe. 3 ml of the oligo- methylhydridosiloxane were injected through the septum and the reaction was stirred. Reaction progress was followed qualitatively by noting onset of catalysis indicated by the formation of an intense royal blue color and, by noting the time required for complete crosslinking (gelation).

NMR Characterization of Polyhydridomethylsiloxane. Oligomethylhydridosiloxane, Me_3Si-$[MeHSiO]_x$-H, (Petrarch/Hüls Corp.) was characterized by NMR to verify the reported molecular weight ($M_n \approx 2,000$ D). From the ^1H NMR integration studies reported in the results section, we calculate an $M_n \approx 1900D$.

Solution Polymerization of Polyhydridomethylsiloxane.

To a 500 ml Schlenk flask are added 50 ml of Me_3Si-$[MeHSiO]_x$-H and 250 ml of freshly distilled toluene. The solution is degassed by vacuum pumping followed by flushing with N_2. To the degassed solution are added 0.5 ml ($\approx 5 \times 10^{-5}$ mol) of ≈ 0.1 M $(h^5\text{-}Cp)_2TiMe_2$ in hexane. After 1 h, the solution turns green and within 2 h the solution turns deep blue. At this point it is allowed to stir for an additional 72 h. Solvent removal by vacuum evaporation results in a viscous liquid which was characterized by ^1H, ^{13}C and ^{29}Si NMR (see below).

Standard Pyrolysis Run. Bulk pyrolyses were performed to obtain samples for combustion analysis or for the DRIFT spectra. These pyrolyses were carried out in a Lindberg furnace (Model No. 58114, single zone) equipped with a Eurotherm temperature controller (Model No. 818S). A 5.00 cm OD (4.44 cm ID) mullite tube, cooled at both ends by means of water circulated through copper coils,

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was inserted into the furnace to protect the heating coils and to provide even heat distribution. Both ends of the tube can be sealed with stainless steel caps and viton o-rings. One cap was fitted with gas inlet and outlet ports to control gas flow rates and pyrolysis atmosphere. Alternately, pyrolyses were conducted in a 3.8 cm OD x 45.7 cm quartz tube, sealed at one end via a quartz cap with a standard o-ring seal. The cap was fitted with gas inlet and outlet ports. The quartz tube was inserted into the mullite tube. This tube was designed for transport of samples in and out of a dry-box.

Tared, half-cylinder, stainless steel pyrolysis boats containing weighed amounts of crosslinked polymer precursor were placed in the quartz tube under the desired atmosphere. The quartz tube with sample was then inserted into the mullite tube so that the samples were in the center of the heated zone (approximately 12 cm in length), usually only 2 or 3 samples fit in this region). The samples were then pyrolyzed by heating, under the desired atmosphere (N_2 or synthetic air), at 5°C/min to the desired temperature. The standard gas flow rate was 0.25 m^3/hr. Sample sizes were typically 200-800 mg. Sample preparation involved placing the crosslinked polymer under vacuum for 2 hr to remove $MeSiH_3$ and traces of hexane.

Results

The work presented here focusses on the properties of a copolymer produced from titanium catalyzed redistribution of methylhydrosiloxanes, -[MeHSiO]$_x$-, reaction (3). Efforts directed towards developing a mechanistic description of the catalytic cycle are reported elsewhere.[12,13] The synthetic methods used to prepare the copolymer are discussed in the experimental section. Brief studies were conducted to optimize the rate and extent of crosslinking in reaction (3), as a means of minimizing reaction time and maximizing ceramic yield. These studies explored the effects of simple modifications at the titanium center and changes in the type of -[MeHSiO]$_x$- precursor on reaction rate and type of product.

These preliminary studies provided sufficient information to choose a "standard polymer" for the subsequent high temperatures studies .

Oligomeric Precursor Survey.

The relative reactivities and extent of crosslinking of the cyclotetramer, (DH$_4$, -[MeHSiO]$_4$-), the cyclopentamer (DH$_5$, -[MeHSiO]$_5$-), and the linear oligomer, Me$_3$SiO-[MeHSiO]$_x$-H (M$_n$ $\approx$ 2000 D) were established using a standard set of reaction conditions (see experimental), and Cp$_2$TiMe$_2$ as the catalyst precursor. The results of these studies are recorded in Table 1. Chemical analysis of the resulting copolymers are shown in Table 2.

Insert Tables 1 and 2

The qualitative reactivities shown in Table 1 indicate that the cyclomers are less reactive than the linear oligomer and that the cyclotetramer reacts slower than the cyclopentamer. However, the chemical analyses (see Table 3) and ceramic yields for the final products are, within experimental limits, identical. We conclude that the crosslink densities of the final copolymers are essentially the same.

Insert Table 3

Given these results, Me$_3$SiO-[MeHSiO]$_x$-H was used in all further studies. The proton NMR of this material contains one resonance for the Si-H proton at 4.69 d and two C-H peaks at 0.10 (major) and 0.18 d (minor). The latter peak is attributed to the Me$_3$SiO- end cap. Proton NMR end group analysis permits calculation of M$_n$ $\approx$ 1,900 D, which is somewhat less than the 2,000 D reported by the supplier. The starting polymer exhibits ^{13}C peaks at 1.04 d (major, by intensity) and at 1.75 d (minor). The ^{29}Si NMR shows one peak at -34.6 d relative to TMS.

Catalyst Survey.

A simple catalyst survey was run using the standard set of reaction conditions described in the experimental section, with the linear oligomer as substrate. We examined the utility of the titanium

complexes: Ti(NMe$_2$)$_4$, Ti(NEt$_2$)$_4$, Cp$_2$TiMe$_2$, CpTiMe$_3$ and, Cp$_2$TiBH$_4$ as catalyst precursors. [Cp$_2$ZrMe(THF)]BF$_4$ was also tested for catalytic activity. These complexes were chosen because they are synthesized readily via literature procedures or are available commercially.

Of the precursors tested, only Ti(NMe$_2$)$_4$, Cp$_2$TiMe$_2$ and CpTiMe$_3$ exhibit any activity. The CpTiMe$_3$ precursor gave the most active catalyst of the three precursors, catalyzing complete gelation in a matter of 10-15 minutes at 0°C with a ceramic yield of ≈ 80%. The Ti(NMe$_2$)$_4$ derived catalyst was the slowest giving incomplete reaction even after 5 days at room temperature. Cp$_2$TiMe$_2$ proved to be the best precursor of all, despite the high activity of CpTiMe$_3$. This is because CpTiMe$_3$ is not stable at room temperature and is even difficult to handle at 0°C. Solid Cp$_2$TiMe$_2$ is also labile and turns black by an auto- catalytic decomposition process even under N$_2$ at -20°C. However, hexane solutions of Cp$_2$TiMe$_2$ remain stable, at liquid N$_2$ temperatures, for up to one week and provide a convenient method of adding the precursor to -[MeHSiO]$_x$-.

Initiation of catalytic redistribution is always preceded by an induction period prior to generation of the active, royal blue catalyst system. This induction period is typically 30-45 minutes if one uses freshly prepared, recrystallized Cp$_2$TiMe$_2$. Thorough degassing of the precursor solutions or liquids is mandatory before reproducible initiation can be obtained.

The standard reaction used to obtain the data in Tables 1-3, and for most of the studies described below, leads directly to intractable gels that cannot be further characterized by solution techniques. To complement the extensive solid state NMR studies described below, we attempted to prepare soluble forms of the methylsilsesquioxane polymer as a prelude to solution NMR studies. To this end, we find that soluble polymers can be obtained by running the reactions in toluene, if sufficient dilution is used. Initial experiments with 1:1, 3:1 and even 4:1 toluene:-[MeHSiO]$_x$- volume ratios led to gel-like products. However, at 5:1 volume ratios and 72 h of reaction at room temperature (following initiation), stable solutions of a copolymer (primarily polymethylsilsesquioxane) were obtained. Vacuum evaporation of the toluene leads to a semi-tractable polymer that slowly "sets" to a rigid solid. If this polymer is immediately redissolved in CDCl$_3$ then NMR characterization can follow.

NMR Characterization

NMR characterization of a wide variety of siloxane units has already been described in the literature.[17] The studies described here will use the standard literature nomenclature and peak assignments as listed in Table 4.

Insert Table 4

The ^{29}Si spectrum for solution polymerized -[MeHSiO]$_x$- contains broad peaks at -33.5, -34.4, -35.9 d for MeHSiO and, -57.2 and -65.5 d for MeSi(O)$_{1.5}$. The ^{13}C spectrum exhibits peaks at 1.68 [(CH$_3$)$_3$SiO], 0.66 (CH$_3$HSiO) and -3.27 d [CH$_3$Si(O)$_{1.5}$]. The proton NMR shows peaks at 4.68 MeHSiO, 0.18 [(CH$_3$)$_3$SiO], 0.13 [CH$_3$Si(O)$_{1.5}$] and 0.10 d CH$_3$HSiO. The NMR results indicate that

the product is a copolymer whose composition is: $[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$.[18] This compares well with the gel composition established by solid state NMR as presented below. The results are supported by the combustion analyses listed in Table 2.

High Temperature Studies of Copolymer - $[MeHSiO]_{0.30}[MeSi(O)_{1.5}]_{0.70}$-.

-$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$-, henceforth copolymer, was chosen as a "standard polymer" for these studies because it is easily and reproducibly prepared by titanium catalyzed redistribution of neat -$[MeHSiO]_x$- or toluene solutions of -$[MeHSiO]_x$-.

The copolymer was further characterized by TGA (Figure 1), DTA , FTIR and NMR. Chemical analyses were obtained for the polymer at room temperature and after heating to 200, 400, 600, 800 and 900°C at 5°C/min under N_2 and following a one hour hold at each temperature. The analysis at each temperature is also shown in Figure 1. Within the error limits of analysis, there is no difference between the elemental analyses at 800 and 900°C. The 900°C analysis is very similar to that obtained by Fox et al for pyrolysis of -$[MeSi(O)_{1.5}]_x$- prepared by hydrolysis of $MeSiCl_3$.[5]

The DTA data does not suggest any significant events that could be used as further support for the other methods of analysis. Occasionally, a small exotherm is seen at 630-670°C (in air); although this exotherm is not found in aged polymer. This exotherm most likely arises from oxidation of residual Si-H bonds.

Insert Figures 1 and 2

Diffuse reflectance infrared spectra (DRIFTS) were also taken both at room temperature and for the 200, 400, 600, 800, and 1000°C samples. The DRIFTS data are presented in Figure 2. The pertinent IR absorptions for the DRIFTS data are recorded in Table 5. ^{29}Si, ^{13}C and ^1H magic angle spinning (MAS) and cross polarized (CP) NMR spectra were also recorded at each temperature. The solid state proton spectra reveal very little, except the presence of Si-Me and Si-H at lower temperatures and, a small peak for Si-H plus a broadened peak for saturated C-H adjacent to Si at temperatures ≥800°C. The ^{29}Si MAS and CP spectra and, the CP ^{13}C spectra for the various temperatures are shown in Figures 3-5. Figure 6 shows the quantitative evolution of the various species based on the ^{29}Si MAS spectra. The peaks in Figures 3 and 4 can be readily assigned to different silicon units based on the literature values listed in Table 4.[17]

Insert Table 5 and Figures 3-6

General Observations

The TGA reveals that much of the weight loss (20%) occurs below 400°C. The chemical composition for the 400°C product is identical to that calculated (Table 2) for pure -$[MeSi(O)_{1.5}]_x$-. Thus, the low temperature weight loss can be ascribed to the disappearance of the -$[MeHSiO]_x$- copolymer segments by depolymerization and volatilization. However, the calculated weight loss

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resulting from complete volatilization of all of the $-[MeHSiO]_x-$ groups would be $\approx 28\%$. Therefore, the disappearance of all of the $-[MeHSiO]_x-$ segments is likely due to some further redistribution together with volatilization. These results have been confirmed by mass spectral analyses (vide infra)

Further heating to 900°C results in an additional weight loss of about 5-7%. The elemental analyses suggest that this loss is due to in part to hydrogen loss above 400°C as this drops from 4.6% to <1% at 900°C. Some loss of carbon is also observed ($\approx 1.8\%$).

The following sections focus on the chemical evolution of the polymer as it is heated to specific temperatures up to 1000°C using the data contained in Figures 1-6 and Tables 2-6.

Room Temperature

The composition of the "standard" polymer precursor, based on MAS solid state ^{29}Si NMR, is $[MeSiO_{1.5}]_{0.65}[MeHSiO]_{0.28}[MeSi(OH)O]_{0.04}[Me_3SiO]_{0.03}$. The proton MAS NMR also reveals the presence of Si-H groups at 4.5 ppm. The ^{13}C MAS spectrum shows two peaks at 1.1 and -2.9 ppm that can be assigned to the DH and T units respectively. These results confirm the solution ^{29}Si NMR studies. The DRIFT spectrum also confirms part of this assignment in that there is a strong nSi-H peak at 2200 cm^{-1}. In addition, the DRIFT spectrum shows sharp vC-H peaks at 2800-2950 cm^{-1} normal for Si-CH$_3$ and a sharp vSi-C absorption (for Si-CH$_3$) at 1260 cm^{-1}. The presence of Me$_3$SiO- and Si-OH moieties cannot be confirmed by DRIFTS because vC-H of the M group is lost in the vC-H of the T and DH units and the small contribution to the spectrum from vSi-OH (3200-3400 cm^{-1}) is lost in the background noise. However, the presence of both are expected given that one can only prepare a well defined (M$_n$ $\approx$ 2000 D) oligomer of $-[MeHSiO]_x-$ by ring opening polymerization of the cyclotrimer, $-[MeHSiO]_3-$, using Me$_3$SiO$^-$ and a water workup.

It would be reasonable to confirm the NMR-determined composition by chemical analysis; however, the error limits for the analysis of preceramics are somewhat higher than for typical organic molecules and do not permit a reliable calculation.[19] All that can be said from the data presented in Table 2 is that the polymer composition does lie between those calculated for $-[MeHSiO]_x-$ and $-[MeSi(O)_{1.5}]_x-$.

200°C

Heating the polymer to 200°C appears to have little effect on the polymer composition as seen in Figure 1. One might expect the Si-OH groups to condense with each other, with Me$_3$SiO- groups or react with Si-H bonds to form Si-O-Si bonds and release H$_2$O, Me$_3$Si-OH or H$_2$. However, the concentrations of these species and their diffusivities are too low for significant condensation to occur. The weight loss in the TGA at 200°C is not reflected by changes in the NMR spectra. This is expected given that the weight loss is approximately 10% which tests the limits of solid state NMR sensitivity . There also are no significant changes in the DRIFTS spectrum.

The data shown in Table 6 list the major (by intensity) fragments observed for electron impact fragmentation of DH$_4$, DH$_5$ and the oligomer. These are compared with the fragments that issue from the copolymer as it decomposes between 150°C and 250°C in the solid probe inlet of the mass spectrometer.

The species suggested to be responsible for the individual m/z fragments are based on literature and our previous studies.[20,21]

Insert Table 6

All of the DH_x species provide fragments indicative of -[MeHSiO]$_x$- where x = 1-3. For x = 4, we see evidence for M-CH$_3$ only and, nothing identifiable or of significant intensity for x > 4. In the solid probe experiments, with the copolymer heated to 150°C, we also see the same fragments for -[MeHSiO]$_x$- where x = 1-3. However, the fragment of major intensity is m/z = 74 found frequently for M-CH$_3$ for the Me$_3$SiO- group. At 250°C, the decomposition products from the copolymer include the same set of fragments for -[MeHSiO]$_x$- where x = 1-3 as found at 150°C but with much less contribution from the m/z = 74. The x = 2 fragment (m/z =120) now predominates in the spectrum. Also of importance is the appearence of fragments m/z = 45, 46 and 90. These can be attributed to MeH$_2$Si, MeSiH$_3$ and (MeH$_2$Si)$_2$ and are products likely to arise from redistribution of the -[MeHSiO]- groups. Consequently, they offer evidence that low temperature weight loss (<400°C) results because of coincidental depolymerization and redistribution, as suggested above.

400°C

At this temperature, the TGA indicates a weight loss of 20% and the chemical analysis data suggest that the only material remaining is -[MeSi(O)$_{1.5}$]$_x$-. Chemical analysis is insufficiently accurate to permit one to draw indisputable conclusions concerning chemical makeup;[19] however, the DRIFTS data are in keeping with the almost complete elimination of Si-H bonds as witnessed by the significant loss of intensity of the n Si-H absorption in the DRIFTS. This loss, as discussed above, is due both to depolymerization and redistribution of -[MeHSiO]$_x$- segments.

The less sensitive ^{29}Si MAS and ^{1}H NMR spectra suggest that the 400°C sample is composed entirely of -[MeSi(O)$_{1.5}$]$_x$-. The use of cross polarization techniques (Figure 4) confirms the DRIFT spectrum by revealing remnants of -[MeHSiO]$_x$- and a very small amount of -[MeSi(OH)O]-. The ^{13}C spectrum has changed somewhat in that the peak at 1.1 ppm is reduced to a shoulder on the major peak which has shifted somewhat from -2.9 to -3.5 ppm.

The stability of polymethylsilsesquioxane is not unexpected given that [MeSi(O)$_{1.5}$]$_8$ is stable to ≈ 415°C.[9]

600°C

The transition between 400 and 600°C results in some chemical changes in the 400°C polymer structure. The [29]Si spectrum reveals a decrease in the number of T units to approximately 65% (from ≈ 100%), coincident with the appearence of peaks for D-type [MeSi(CH$_x$)O] units (14%) and Q (20%) units (see Figure 6). Given that the relative amounts of each are reasonably close, these species most probably arise by direct redistribution of the T groups. Partial oxidation by adventitious oxygen could account for the slightly higher abundance of the Q groups. This is supported by the slight reduction in carbon content in the chemical analysis (Figure 1).

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The ^{13}C NMR spectrum shows some changes as the peak attributable to Si-CH_x species broadens, shifts to -4.2 ppm and becomes asymmetric. This is in keeping with the formation of new D-type units in the polymer matrix. In the DRIFT spectrum, the vC-H absorptions are still fairly sharp although diminished compared to the nSi-O absorptions. The vSi-CH_3 peak at 1260 cm^{-1} is still sharp, although somewhat diminished in intensity. Careful inspection of the region adjacent to nSi-CH_3 reveals the appearence of a small peak at ≈1360 cm^{-1}. Yajima et al[22] have shown that this peak,[19b] which is never very intense, corresponds to the formation of the Si-CH_2-Si linkage which corroborates the appearence of new D-type units in the polymer matrix.

Neither the DRIFT spectrum nor the NMR studies provide evidence for either Si-H or SiO-H bonds.

Although, the 600°C material has reacted in part, the evidence still suggests that much of the 400°C structure is retained. This conclusion is supported by contrast with the very drastic changes that occur on further heating to 800°C.

<u>800°C</u>

At this temperature, all the analytical tools reveal major changes in the structure of the material. The chemical analysis in Figure 1 shows that most of the hydrogen has been driven off; although, the C:Si ratio remains essentially unchanged. In the NMR spectra, all of the peaks broaden greatly. The presence of Q units becomes significant, the number of T units continues to decrease (42%). The most important observation is the reappearence of DH units in the ^{29}Si spectrum and in the ^{1}H NMR spectrum (Si-H). The ^{13}C spectrum provides limited information at this stage because the peak becomes extremely broad (typical of a disordered material) and shifts its center to 5 ppm. Furthermore, slight peaks begin to appear at higher field that are indicative of amorphous or graphitic carbon.[23-25] Cross polarization cannot be used to enhance these signals because the average number of protons that remain in the sample have dropped considerably, as noted above. Efforts to distinguish between graphitic and amorphous carbon using Raman spectroscopy are under way.[24]

The DRIFT spectrum confirms the reappearance of the Si-H bonds (vSi-H at ≈ 2200 and 2254 cm^{-1}). In addition, the 800°C DRIFT spectrum exhibits well developed absorptions for n SiO-H at ≈ 3200-3400 cm^{-1}. These absorptions were readily confirmed by exposing a sample of the pyrolyzed material to D_2O overnight. Following exchange of D for H, the absorption at 3200-3400 cm^{-1} is considerably diminished and new absorptions appear at 2200-2400 cm^{-1} that correspond to v SiO-D.

<u>1000°C</u>

The DRIFTS and the ^{29}Si MAS NMR spectra show that this sample has essentially the same chemical organization as the 800°C material. The only significant difference is in the hydrogen content of the material as revealed by our inability to obtain good CP MAS [29]Si spectra. The ^{29}Si MAS NMR spectrum indicates that the composition of this material is SiO_4 (35%), SiO_3C (42%) with some SiO_2C_2 (<10%)and SiO_2CH (<20%) units. <u>Given the fact that the Si:C ratio has not changed in the 800°C or 900°C chemical analyses and remains approximately 1:1, we must conclude that some of the carbon is no longer bonded directly to silicon and has segregated to form small pockets of graphitic or amorphous</u>

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The formation of free carbon during pyrolysis of silsesquioxanes has been discussed by Fox et al,[5] Baney et al[6] and is in keeping with Babonneau et al's[25] studies on the pyrolytic evolution of D/Q copolymers produced by sol-gel processing . It also is in keeping with our results on the pyrolytic evolution of -[MeNH$_2$Si]$_x$- (under N$_2$) at temperatures above $\approx$ 600°C wherein ^{29}Si NMR shows evidence for exclusive formation of Si$_3$N$_4$ and ^{13}C NMR provides evidence for free carbon.[26]

Black Glass

SEM images of fragments of a bulk sample of the standard polymer that has been heated to 900°C according to the standard heating schedule reveal essentially featureless materials that are amorphous and pore free at the highest magnifications possible. XRD analyses of crushed samples of this material are also featureless in keeping with its amorphous nature.

Discussion

Titanium catalyzed redistribution of either cyclomeric or oligomeric methyldhydridosiloxanes neat or in toluene produces a copolymer of almost constant composition, {-[MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$-}, if the reaction is run neat or long enough (72-96 h) in toluene. The 5:1 toluene solutions are normally stable for at least 120 h. Beyond this period, gelation is observed occasionally, especially if excess catalyst is used.

The fact that the system does not attain complete redistribution is predictable. As the degree of crosslinking increases, the mobility of the catalyst in the polymer decreases significantly and the concentration of reactive monomer units, -[MeHSiO]-, available for crosslinking and redistribution decreases accordingly. Therefore, the reaction must slow and eventually stop short of completion.

The fact that it stops in essentially the same place for the cyclomeric and oligomeric reactants is not unexpected. The only likely difference with the cyclomeric reactants is the initial ring opening step which accounts for their exhibiting slightly poorer rates of reaction as compared with the oligomeric reactant.

High Temperature Studies of Copolymer - [MeHSiO]$_{0.30}$[MeSi(O)$_{1.5}$]$_{0.70}$-.

The high temperature studies described here were conducted to: (1) develop an understanding of the stability of the methylsilsesquioxane copolymer produced via reaction (3); (2) identify modes of decomposition for comparison with the decomposition patterns of -[MeHSiNH]$_x$- and -[H$_2$SiNMe]$_x$- and (3), detail the chemical transformations that the copolymer undergoes during heating to temperatures up to and including 1000 °C for comparison with previous studies on the pyrolysis of sol-gel derived -[MeSi(O)$_{1.5}$]$_x$- polymers.[5]

On heating to 400°C, the copolymer loses approximately 20 weight percent which is associated with the disappearence of almost all of the starting monomer units. At this point, the polymer consists almost entirely of methylsilsesquioxane or T units as supported by all of the characterization methods employed. Consequently, all of the chemistry that occurs above 400°C can be ascribed to reactions of T groups.

This chemistry is directly associated with the conversion of the polymer to an amorphous $Si_xO_yC_z$ network, "black glass"[5,6] and free carbon. These same methods suggest that little chemistry occurs below or at 600°C.

Above 600°C, e.g. at 800°C, all of the characterization techniques, except elemental analysis, indicate a drastic change in the solid state structure of the polymer. The 800°C spectra all show very significant broadening of peaks. One explanation for the observed broadening is that the polymer is transformed from a partially crosslinked material, where relatively free motion of individual chain segments is possible, : highly crosslinked network where motion is very restricted. This leads to diminished degrees of freedom for specific chain segments and therefore a larger distribution of absorbing species. This explanation is reasonable if the polymer structure remains intact; however, the 800°C infrared spectrum suggests otherwise. For example, n Si-C (1260-1270 cm^{-1}) is a sharp, easily identified absorption feature common to all methylpolysiloxanes. It is clearly visible in all of the spectra below 800°C, but visible only as a shoulder in the 800°C spectrum. Consequently, highly restricted chain segment motion as a cause of spectra broadening can serve only as a partial explanation.

The loss in the intensity for n Si-C suggests an alternate explanation wherein the T groups react almost completely with each other on heating to 800°C. The resulting spectral changes must then be associated with a multitude of solid state reaction products wherein only some part of the original polymer structure is maintained. This reorganization occurs coincident with a significant loss ($\approx$ 3%) in hydrogen content (Figure 1).

The chemical changes associated with reorganization include the reappearence of both Si-H and Si-OH units and, formation of quantities of Q and D-type or [MeSi(CH$_x$)O] units. To form new bonds, we must break either C-H, Si-C or Si-O bonds. To form Si-H and Si-OH bonds and new Si-C bonds (D units), we must break both C-H and Si-O bonds. Clearly, we must also cleave Si-C bonds to make Q groups. The exact bond breaking and bond making sequence(s) whereby these reactions occur is not immediately evident. That is, does Si-C bond cleavage occur as a consequence of the formation of new Si-H and/or Si-OH bonds or after the fact.

Without detailed labelling and kinetic studies it is not possible to delineate the exact reaction pathways whereby T groups react with each other at elevated temperatures. However, it is possible to make several basic observations based on literature precedent.

To begin with, at temperatures above 600°C, the ^{29}Si, ^{13}C NMR and DRIFT spectra ($\approx$ 1360 cm^{-1} deformation) indicate that one reaction pathway open to T groups leads to the formation of Si-CH$_x$-Si- units. Based on Yajima et al's work with polycarbosilanes,these linkages will likely lead to the formation of SiC on heating to higher temperatures.[19b,22] Fox et al.[5] report that heating methylsilsesquioxanes to temperatures of 1500°C does indeed lead to the formation of SiC.

The ^{29}Si integration data plotted in Figure 6, when considered in terms of the elemental compositions for the bulk materials, indicate that a second major reaction pathway must exist for the disappearence of T groups. At the highest temperatures, we observe that the quantity of Q groups ($\approx$ 35%) is more than

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twice the number of D groups (<10%). Furthermore, the bulk analyses of the materials at 800°C and 900°C are essentially identical (Table 3) and, the silicon to carbon ratio does not change significantly from 400°C to 900°C. The appearence of Q groups indicates that Si-C bonds are cleaved without being reformed. The fact that the carbon content does not coincidently drop off is further support for the formation of free carbon as suggested above.

This free carbon probably derives from initial coupling of methyl groups as observed during vapor pyrolysis of tetramethylsilane.[27] The exact nature of this carbon (graphitic or amorphous)[23,24] cannot be deduced in the present study by MAS ^{13}C NMR; however, we have observed a similar product in pyrolysis studies of the -[H_2SiNMe]$_x$- polymers.[26]

At present, we would like to suggest that the materials formed on heating polymethylsilsesquioxanes to temperatures in the range of 600 to 1000^{+}°C are best described as glasses or solid solutions. These glasses may, on extended heating in the same temperature range or heating to higher temperatures, form known ceramic materials. We will explore this concept again in another paper that focusses on the high temperature chemistry of polymethylsilazanes.[26]

Comparison with Sol-Gel Derived Polymethylsilsesquioxanes

Pyrolysis of the crosslinked polymers of Table 1 in nitrogen to 900°C permits us to compare our polymethylsilsesquioxane with the one prepared by Fox et al. [5] We find, as does Fox et al, that pyrolysis produces a "black glass". The compositions of the 900°C materials produced in both studies are listed in Table 5 with the apparent ceramic compositions. Within the error limits of the analytical technique, the compositions and the ceramic yields of the black glasses produced by both methods are very similar.

We have also examined the pyrolysis of the polymethylsilsesquioxane in an oxygen atmosphere to determine the effects of oxidation on the type of product obtained. As expected, the product is primarily SiO_2 with some excess hydrogen. The ceramic yields for all the polymers are 91 ± 1 %. Calculated ceramic yields for reaction (6) are 90 %.

$$\text{-[MeSi(O)}_{1.5}]_x\text{- + O}_2 \xrightarrow{\quad \Delta \quad} SiO_2 + 1.5H_2O + CO_2 \qquad (4)$$
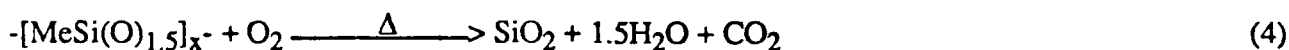
Consequently, we note that the titanium catalyzed crosslinking and redistribution reactions of -[MeHSiO]$_x$- cyclomeric and oligomeric polysiloxanes lead to inorganic polymers which have numerous similarities to those produced by typical sol-gel processing. Moreover, pyrolysis of these preceramics leads to ceramic products apparently identical to those obtained by pyrolysis of the sol-gel processed material.

Future work in this area will examine the utility of titanium catalyzed redistribution for the synthesis of other silsesquioxanes.

Acknowledgements

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18. This integration is confirmed by a novel alcoholysis reaction in which methanol is added directly to the active catalyst solution:

$$-[\text{MeHSiO}]- \text{MeOH} \xrightarrow{\text{"Ti"/RT}} H_2 + -[\text{Me(MeO)SiO}]_x-$$

^{1}H NMR integration of this polymer shows [Me(MeO)SiO]:[MeSi(O)$_{1.5}$] ratio of 3:7 in keeping with the solid state results. Rahn, J. A. and Laine, R. M.; and Zhang, Z-Fan in <u>Polymer Based Molecular Composites</u>. Schaefer, D. W. and Mark, J. E.; Eds, Mat. Res. Soc. Symp. Proc., Vol *171*, **1990** p 31.

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23. The ^{13}C NMR relaxation times for carbon without hydrogen attached can be of the order of minutes to hours (especially for graphitic carbon, ≈ 120 ppm). Consequently, identification of these species using NMR techniques is difficult without a dedicated instrument.

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27. see for example <u>Carbosilanes. Synthesis and Reactions</u>, Springer-Verlag, Fritz, G. and Matern, E. Berlin, **1986**.

Substrate	Reaction Time	Product Physical Characteristics	Ceramic[a] Yield (wt %)
-[MeHSiO]$_4$-	3-4 hr	Very Viscous in 1 hr Hard Plastic in 3-4 hr	78
-[MeHSiO]$_5$-	15 min-1 hr	Hard Plastic	79
-[MeHSiO]$_x$- M$_n \approx$ 2,000 D	10-15 min	Hard Plastic	81

Table 1. Polymerization of Methylhydridosiloxane Substrates by Cp$_2$TiMe$_2$ at Ambient Temperature. a. Ceramic yields were determined using thermogravimetric analysis. Heating rate was 5°C/min to 900°C in N$_2$. Reproducibility of the ceramic yields is ± 5%.

Substrate	C	H	N	Si	O[a]	
-[MeHSiO]$_4$-	19.45	5.62	0.00	43.60	31.33	
-[MeHSiO]$_5$-	20.37	5.98	0.00	45.11	28.54	
-[MeHSiO]$_x$- M$_n \approx$ 2,000 D	17.93	4.45	0.11	40.66	36.85	
-[MeSi(O)$_{1.5}$]$_x$-	17.90	4.50	---	41.84	35.76	calc.
-[MeHSiO]$_x$-	19.98	6.71	---	46.71	26.61	calc.

Table 2. Combustion Analysis of Copolymer Formed By Reaction of Methylhydridooligosiloxane Precursors with Cp$_2$TiMe$_2$ at 21°C. a. Oxygen is determined by difference.[19]

Substrate	C^a	H	N	Si	O^b	Ceramic[c,d] Composition
-[MeHSiO]$_4$-	16.35	0.73	0.14	45.71	37.07	SiO_2 = 70 % SiC = 19 % C = 11 %
-[MeHSiO]$_5$-	16.43	0.96	0.04	45.00	37.57	SiO_2 = 70 % SiC = 21 % C = 9 %
-[MeHSiO]$_x$- $M_n \approx 2,000$ D	15.87	1.18	0.05	46.08	36.82	SiO_2 = 69 % SiC = 20 % C = 10 %
MeSi(O)$_{1.5}^e$	14.3	-.-	-.-	43	--.--	

Table 3. Combustion Analyses[19] of the 900°C Pyrolysis Product of the Copolymer Derived From Various -[MeHSiO]$_x$- Precursors.

a. Titanium analyzed in representative samples gave an average value of 0.1%. b. Oxygen is determined by difference. c. Pyrolyses were conducted in N_2 at a heating rate of 5°C/min. d. Apparent ceramic composition was determined using silicon as the limiting element. e. Results from Fox et al[5]

Si Unit		Chemical Shift (ppm vs TMS)
Me_3SiO-	M	+6 to 7
HMe_2SiO-	MH	-5 to 7
$HOMe_2SiO-$	MOH	-11 to -12
$-[Me_2SiO]-$	D	-20
$-[MeHSiO]-$	DH	-35 to -37
$-[MeSi(OH)O]-$	DOH	-55
$-[MeSi(O)_{1.5}]-$	T	-65 to -67
$-[HSi(O)_{1.5}]-$	TH	-85
$-[Si(O)_2]-$	Q	-100 to -110

Table 4. [29]Si Chemical Shifts for Common Si Units. Reference 17.

	νO-H	νC-H	νSi-H	νC=O	νSi-C	νSi-O
RT	3729vw?	2969s 2910	2166s	--	1266vs 781vs	1039vs
200°C	3734vw?	2969s 2910	2167s	--	1267vs 783vs	1041vs
400°C		2971s 2915	2166w	--	1269s 778vs	1132vs 1039vs
600°C		2969m 2913w	--	1732w	1269m 791vs	1047vs
800°C	3644- 3324 mvbr	2925w	2257w 2200w	1732w	1269sh	1037vs 1049vs
1000°C	3644- 3324 mvbr	3028w 2925w 2857w	2266w 1890w	--	--	1053vs

Table 5. Selected Infrared Absorptions for Copolymer at Various Pyrolysis Temperatures. All absorptions are reported as cm^{-1}. Pyrolyses were conducted in N$_2$ at a heating rate of 5°C/min.

Fragment	m/z	DH4[a]	DH5[a]	oligomer[a]	[MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$	
					150°C[a]	250°C[a]
MeSiH$_2$	45				40	
MeSiH$_3$	46				≈3	36
MeHSiO	60	10	18	15	17	67
Me$_2$SiO	74				100	98
(MeSiH$_2$)$_2$	90					30
(MeHSiO)$_2$	120	12	06	≈2	8	100
DH$_3$	180	20	17	13	5	60
DH$_4$	240	61	100	100		
DH$_5$-Me	285	--	78	82		

Table 6. Mass Spectral Fragmentation Patterns and Intensities for DH$_4$, DH$_5$, Me$_3$SiO(MeHSiO)$_x$-H and, Fragments Found on Heating [MeHSiO]$_{0.3}$[MeSi(O)$_{1.5}$]$_{0.7}$ to 150 and 250°C. a. all intensities are relative to highest peak in each spectrum.

Captions for Figures 1-6

Figure 1. Thermogravimetric Analysis of -$[MeHSiO]_{35}[MeSi(O)_{1.5}]_{.65}$- as a Function of Temperature. The TGA heating schedule was 5°C/min in N_2. Bulk samples for the analyses were heated in a similar manner.
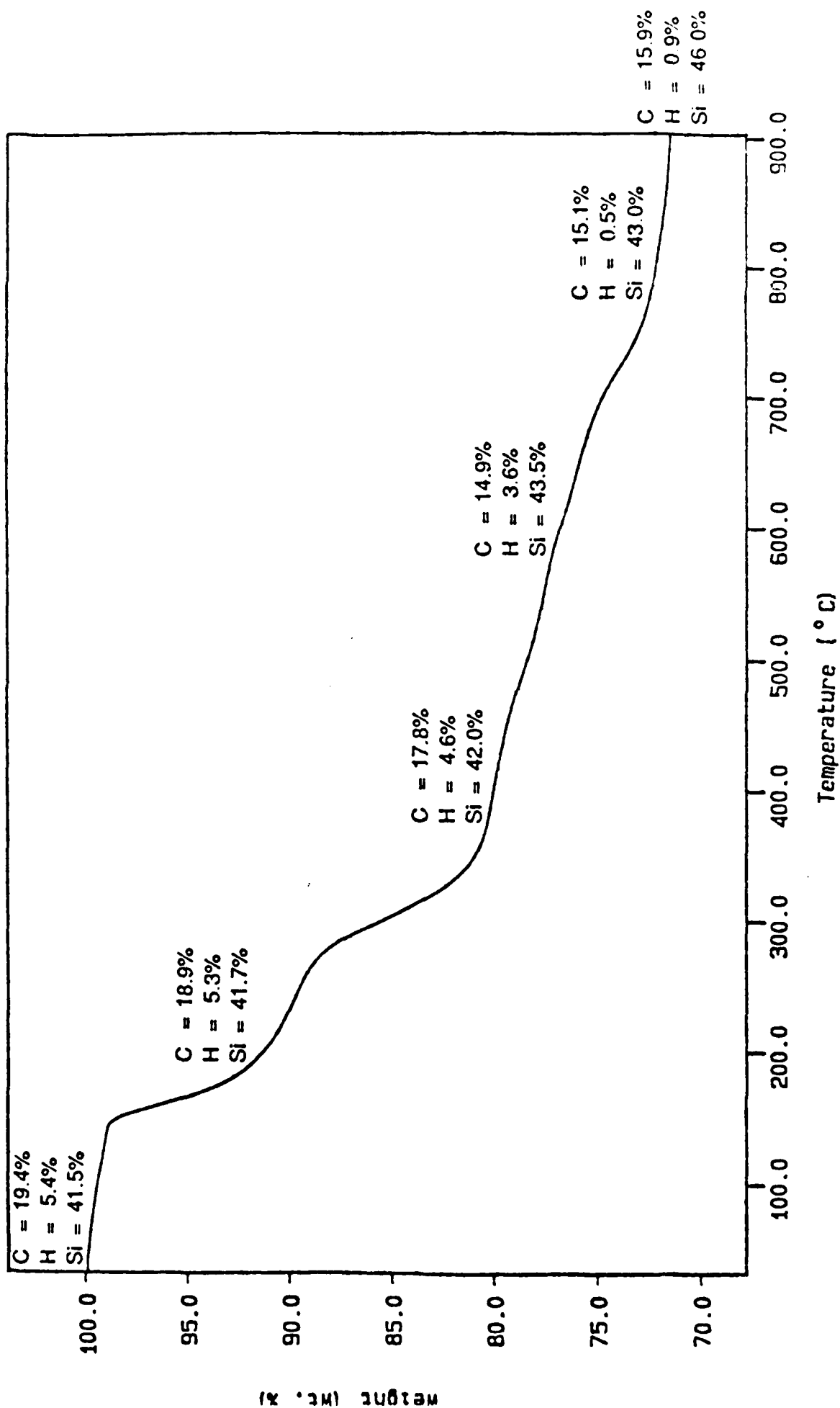
Figure 2. Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) of -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- Following Heating to Selected Temperatures. Samples heated at 5°C/min in N_2 to the desired temperature, mixed with KBr (under N_2). Spectra taken under N_2.

Figure 3. ^{29}Si MAS NMR Spectra of -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- Following Heating to Selected Temperatures. Samples were heated at 5°C/min in N_2 to the desired temperature and crushed under N_2 and transferred to NMR rotors under dry box conditions.
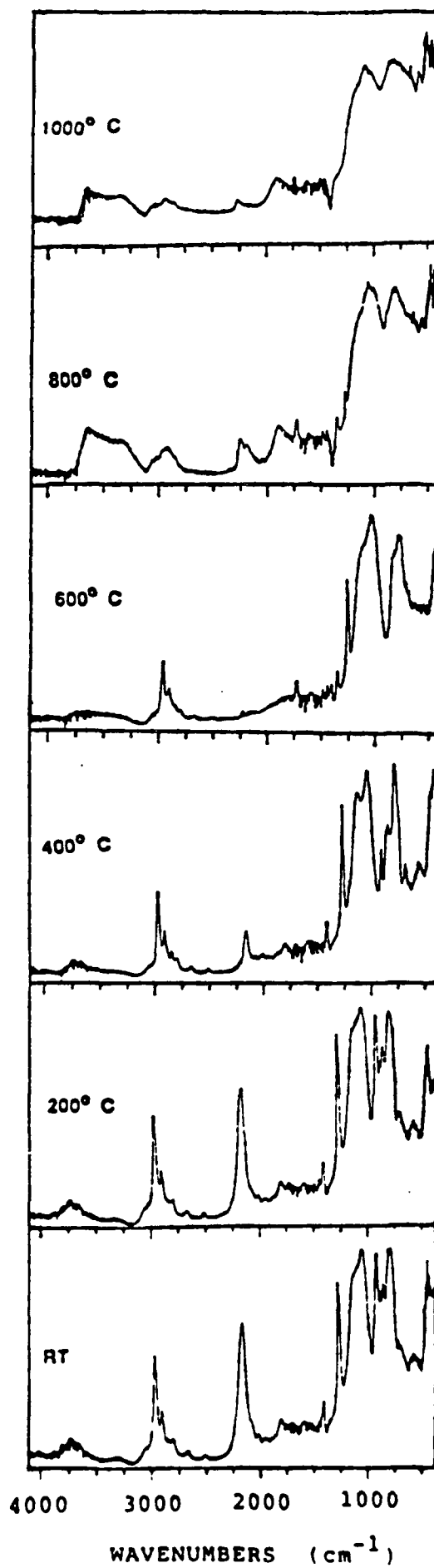
Figure 4. ^{29}Si CP MAS NMRs of -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- Following Heating to Selected Temperatures. Samples were heated at 5°C/min in N_2 to the desired temperature and crushed under N_2 and transferred to NMR rotors under dry box conditions.
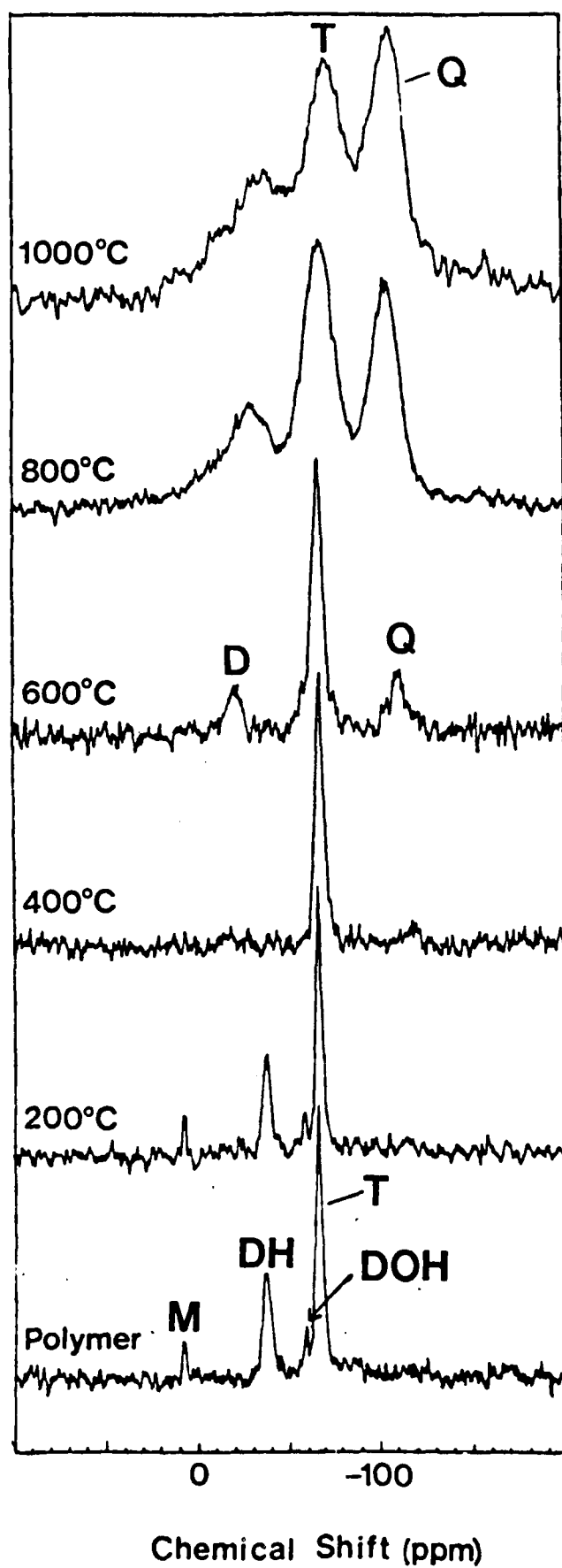
Figure 5. ^{13}C CP MAS NMRs of -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- Following Heating to Selected Temperatures. Samples were heated at 5°C/min in N_2 to the desired temperature and crushed under N_2 and transferred to NMR rotors under dry box conditions.

Figure 6. Changes in Quantities of Various Silicon Species as a Function of Temperature. Determined by ^{29}Si MAS NMR Spectra Following Heating of $[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$ to Selected Temperatures.

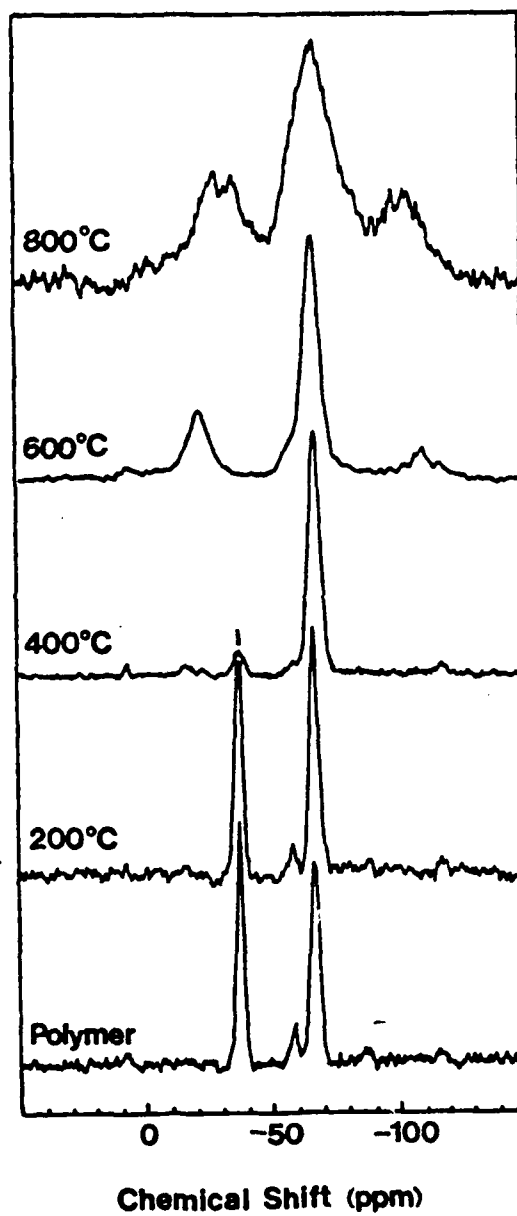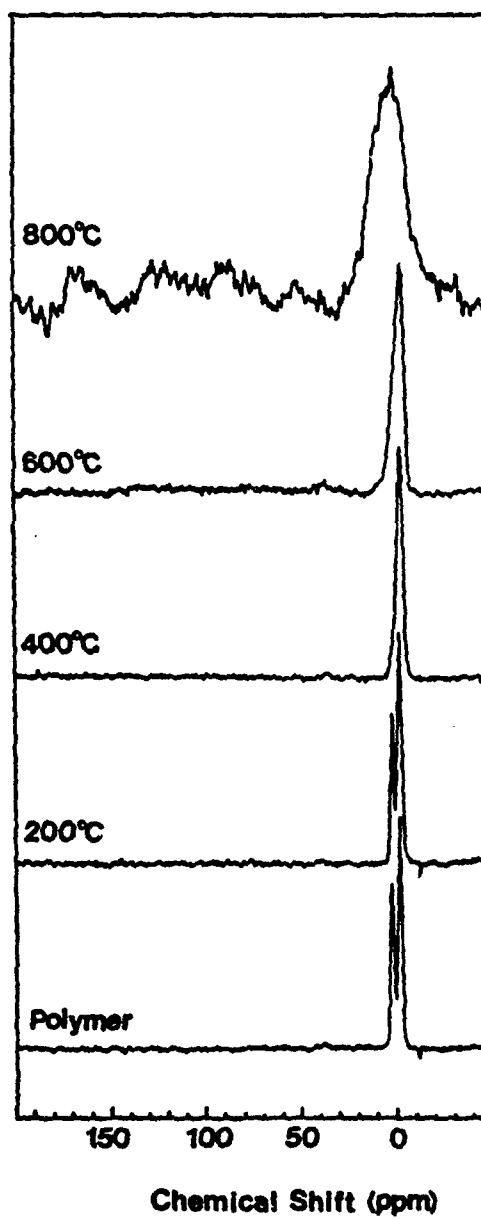The figure shows a thermogravimetric analysis (TGA) curve plotting weight (wt, %) on the y-axis (ranging from 70.0 to 100.0) versus Temperature (°C) on the x-axis (ranging from 100.0 to 900.0).

C = 19.4%
H = 5.4%
Si = 41.5%

C = 18.9%
H = 5.3%
Si = 41.7%

C = 17.8%
H = 4.6%
Si = 42.0%

C = 14.9%
H = 3.6%
Si = 43.5%

C = 15.1%
H = 0.5%
Si = 43.0%

C = 15.9%
H = 0.9%
Si = 46.0%

ABSORBANCE

WAVENUMBERS (cm^{-1})

T
Q

1000°C

800°C

D
Q
600°C

400°C

200°C

T

DH
DOH
M
Polymer

0   -100

Chemical Shift (ppm)

800°C

600°C

400°C

200°C

Polymer

0   -50   -100

Chemical Shift (ppm)

Figure 4

800°C

600°C

400°C

200°C

Polymer

150   100   50   0

Chemical Shift (ppm)

Figure 5

Figure D#6